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PROCEEDINGS

VOLUME I:

FEATURE PRESENTATIONS
ENVIRONMENTAL TRANSPORT AND FATE
ENVIRONMENTAL EFFECTS
ENVIRONMENTAL MANAGEMENT OPTIONS

THE MULTI-MEDIA APPROACH: Integrated Environmental Protection

November 25 & 26, 1991
Four Seasons
Inn on the Park
Toronto, Ontario
Canada

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VOLUME I

FEATURE PRESENTATIONS

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Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1991 Technology Transfer Conference are published in two volumes of conference proceedings corresponding to the following sessions:

VOLUME I: FEATURE PRESENTATIONS
ENVIRONMENTAL TRANSPORT AND FATE
ENVIRONMENTAL EFFECTS
ENVIRONMENTAL MANAGEMENT OPTIONS

VOLUME II: FEATURE PRESENTATIONS
EMISSIONS AND EFFLUENTS
ENVIRONMENTAL TECHNOLOGIES PROGRAM
PREVENTION, TREATMENT AND REMEDIATION
TECHNOLOGIES/BIOTECHNOLOGY

Volume I is comprised of presentations given during Session A, Session B and Session C of the conference, as well as all Feature Presentations.

For reference purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4649 or 323-4573

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GP15 A Study of Chemical Interferences in the Analysis of N-Nitrosodimethylamine in Environmental Samples; V.Y. Taguchi, E.J. Reiner, D.T. Wang, J-P. Palmentier and S.W.D. Jenkins, Environment Ontario, Rexdale, Ontario 720

GP16 A Turn-Key FTIR System for the Analysis of Gas Phase Polychlorinated Biphenyls; J. Semmler, P. Yang and G. Crawford, Environment Ontario, Rexdale. Ontario 724

GP17 National Research Council Marine Analytical Chemistry Standards Programs — Certified Reference Materials; S. Berman, National Research Council Canada. Ottawa. Ontario 731

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U.S.A.

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Environmental Transport and Human Exposure: A Multimedia Approach in Health-Risk Policy

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Introduction

In his treatise *Air, Water, and Places*, the ancient-Greek physician Hippocrates demonstrated that the appearance of disease in human populations is influenced by the quality of air, water, and food; the topography of the land; and general living habits. This approach is still relevant and, indeed, the cornerstone of modern efforts to relate public health to environmental factors. What has changed is the precision with which we can measure and model these long-held relationships. Today, environmental scientists recognize that plants, animals, and humans encounter environmental contaminants via complex transfers through air, water, and food and use multimedia models to evaluate these transfers. In this talk, I explore the use of multimedia models both to examine pollution trends and as a basis for characterizing human health risks and ecological risks. The strengths and weaknesses of the approach are discussed.

I begin with a review of multimedia models—how they came about and where they are going. I highlight areas of success, areas of weakness, and areas that need much more work—such as plant-soil-air modelling. Next, I look at recent efforts to integrate multimedia models with exposure models to develop a more complete picture of human exposure to environmental contaminants. This is followed some ideas about the formal treatment of uncertainty in multimedia models and how this could bring about a better understanding of their precision and accuracy. Finally, I will discuss some new directions for multimedia model research.

Multimedia Models

Efforts to assess human exposure from multiple media are not particularly new. The need to assess human exposure to global fallout in the 1950's led rapidly to a framework that included transport both through and among air, soil, surface water, vegetation, and food chains. Efforts to apply such a framework to nonradioactive organic and inorganic toxic chemicals have been more recent and have not as yet achieved the level of sophistication extant in the radioecology field.

The first widely used multimedia compartment models for organic chemicals were the "fugacity" models developed by Mackay (1979, 1991) and Mackay and Paterson (1981, 1982). Cohen and Ryan (1985) introduced the concept of the multimedia compartment model as a screening tool with the MCM model. At the Lawrence Livermore National Laboratory (LLNL), we have developed a multimedia screening model, called GEOTOX (McKone and Layton, 1986), which was one of the earliest multimedia models to explicitly address human exposure for nonradioactive contaminants.

In a multimedia model we lump major components of the environment into homogeneous subsystems or compartments that can exchange mass with other adjacent compartments. Quantities, concentrations, or fugacities within compartments are described by a set of linear, coupled, first-order differential equations, which can be solved under steady-state or dynamic conditions. A compartment is described by its total mass, total volume, solid-phase mass, liquid-phase mass, and gas-phase mass. Mass flows among compartments include solid-phase flows, such as dust suspension or deposition, and liquid-phase flows, such as surface run-off and ground-water recharge. The transport of individual chemical species among compartments occurs by diffusion and advection at the compartment boundaries. Each chemical species is assumed to be in chemical equilibrium among the phases within a single compartment. However, there is no requirement for equilibrium between adjacent compartments. Decay and transformation processes (such as radioactive decay, photolysis, biodegradation, etc.) are treated as first-order, irreversible removals. The compartment structure we are using for assessing the regional impacts of toxic substances in air, water, and soil is illustrated in Figure 1.

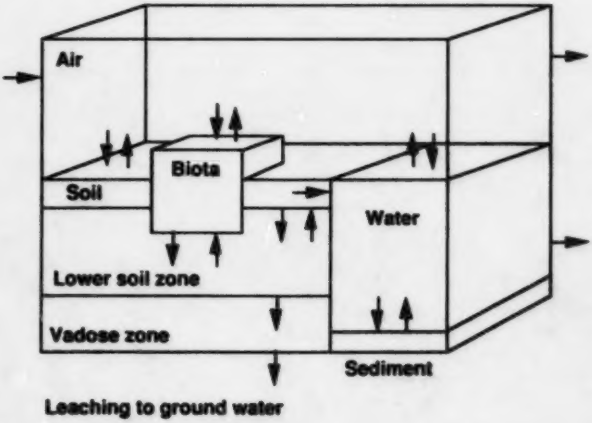

Figure 1. An illustration of mass exchange processes modeled in a seven-compartment environmental transport and transformation model.

Multiple Pathway Exposures

Human exposures to environmental contaminants result from contact with contaminated soils, water, air, and food as well as with drugs and consumer products. The extent of such exposures depends on (1) human factors and (2) the concentrations of a chemical in contact media. Human factors include all behavioral, sociological, and physiological characteristics of an individual that directly or indirectly affect his or her contact with the substances of concern. The principal output of an exposure assessment is a quantitative estimate of contact, expressed as mass of chemical per kg body weight per day. Exposures should be estimated for specific routes (i.e., inhalation, ingestion, and dermal uptake) because route-specific uptake, distribution, and metabolism are accounted for in pharmacokinetic models that could be used in risk assessments.

An early approach for systematically assessing multiple pathway exposures to nonradioactive environmental contaminants is the exposure commitment method (ECM) (Bennett, 1981). Exposure commitments (i.e., contaminant concentration in human tissue) are calculated from transfer factors that are the ratios of the steady-state concentrations of contaminants in the compartments of an exposure pathway. An exposure commitment is determined by multiplying the transfer factors of a given pathway, for example, air—>plants—>livestock—>diet. This method has been applied to organic chemicals and metals. Applications of the ECM are retrospective and depend on measured concentrations of the substances in the different compartments to estimate transfer factors.

McKone and Daniels (1991) have developed an approach that explicitly allows for the estimation of exposures to a substance based on either measured or predicted concentrations of the substance in contact media. Pathway-exposure factors (PEFs) are used to link chemical concentrations in multiple environmental media to human exposure by route—inhalation, ingestion, uptake. Specifically, each PEF numerically translates a chemical concentration in each of the primary environmental media (air, water, and soil) into exposure rates (in mg/kg-d) for each route of exposure. Incorporated into each PEF is information on human physiology and life style, as well as data describing pollutant behavior in food chains or in microenvironments, such as indoor air. In contrast to the ECM, this approach is prospective. This type of prospective approach has been used by Chetty (1991) to assess the impacts of benzene and pyrene in the Los Angeles basin.

Uncertainties

At best, mathematical models only approximate real systems, and therefore their predictions are inherently uncertain. The need to address human exposure in a multimedia framework brings with it a need to characterize the uncertainty in human exposure models and the combined uncertainty in exposure and dose/response models. In characterizing uncertainty in exposure models, three key issues should be considered: (1) uncertainty in predicting the relationship between sources of contaminants and concentrations in the accessible environment; (2) uncertainty in quantifying pathway-exposure factors (PEFs) that relate environmental concentrations to levels of exposure; and (3) the important contributions to the combined uncertainty in environmental dispersion and pathway-exposure factors.

Future Directions

In their efforts to construct new multimedia-exposure models, environmental scientists should recognize the importance of being both comprehensive and realistic in developing exposure scenarios. In addition to an emphasis on comprehensive human exposure modelling and formal treatment of uncertainties, there are four other areas that, I believe, will be important for the future of multimedia models—(1) formal validation studies (2) improved air-plant-soil models, (3) ecological risk assessment, and (4) ecological economics. Little real progress with multimedia models will occur until there is a coordinated effort to validate a multimedia model both with measured data and with other models. The recent literature reveals new understanding about the transfer of contaminants among soil, air, and terrestrial plants and this information needs to be incorporated into the next generation of multimedia models. Also, multimedia models could provide valuable input to the process of calculating ecological risk, but so far the literature in this area is incomplete. Finally, the newly established field of ecological economics (Costanza, 1989), which seeks to address broad-scale relationships between ecosystems and economic systems, is an area well-suited match to the multimedia approach, but the courtship has yet to begin,

Acknowledgements

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Dioxin Analysis State-of-the-Art:
the study of multimedia contaminants

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Introduction

Studies of the sources, transport and fate, and effects of the chlorinated dibenzo-p-dioxins (dioxins) and dibenzofurans (furans) are among the most difficult in environmental research. Central to these investigations are effective analytical methods that can quantify ultra-trace concentrations of dioxins/furans in a wide range of complex sample types. Developments in science as applied to toxic environmental contaminants essentially are the story of the dioxins/furans, as there is a close parallel between advances in analytical methods and advances in the environmental sciences. Because of the numerous studies of dioxins/furans in air, water, soil, industrial emissions, and in human and animal tissue, the dioxins and furans may be considered the first chemicals studied as true multimedia contaminants.

The History of Dioxin and Furan Contamination

Environmental contamination episodes. In 1957 millions of broiler chickens in the U.S.A. died after ingesting toxic compounds in feed fats. It was not until 1966 that one of the toxic compounds was identified as 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin (1,2,3,7,8,9-H_6CDD) by x-ray crystallography. In the 1960's attention was focused on 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) produced as a trace side-product in the manufacture of chlorophenols. Since chlorophenols were used as starting products in the manufacture of a number of industrial chemicals including the widely used herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2,3,7,8-TCDD contamination of the environment became widespread. Incidents such as the spraying of Agent Orange in Vietnam from 1962-1970; the industrial accident at Seveso, Italy in July, 1976; and improper waste disposal at many Missouri sites during the early 1970's that resulted in the 1982 evacuation of the town of Times Beach, received intensive public scrutiny and are now well-documented. The presence of these chemicals in old chemical dump sites such as the Love Canal has also been highly publicized. In 1968 and 1979, cases of human poisoning from accidental ingestion of PCBs occurred in Japan and Taiwan, respectively. The presence of some chlorinated dibenzofurans in the PCBs was thought to be the principal agent responsible for the adverse health effects observed. Other studies showed that furans are formed during the uncontrolled burning of PCBs after a series of PCB-filled capacitor fires occurred in several different countries. One of the most publicized capacitor fires took place in an office building in Binghamton, N.Y. in 1981. Furans are also found in chlorophenols and related industrial chemicals. The above issues are all described in references 1-4.

Other sources of dioxins and furans. In 1977 dioxins were found in the fly ash from municipal waste incinerators in The Netherlands (5). The following year, this finding was confirmed in fly ash from Ontario incinerators (6). In 1979 the New York State Department of Health announced the finding of 2,3,7,8-TCDD in two Lake Ontario fish. The Ontario Ministry of the Environment (MOE) set up a special laboratory to study this issue in October, 1980. By 1981 a data base of a few hundred analyses of 2,3,7,8-TCDD in fish was developed separately by Ontario and by New York State. Since the finding of 2,3,7,8-TCDD in fish showed that some waterborne route of contamination existed, MOE also began testing Lake Ontario surface water and drinking water. MOE's detection limits were 10 parts per trillion (ppt) in fish and 1ppt in 1L water samples (7). In September, 1985, the U.S. EPA found elevated levels of 2,3,7,8-TCDD in a few fish sampled in areas near Pulp & Paper mills. Intensive investigations by MOE during 1985-86 confirmed that dioxins and furans were contaminants of mills that employed chlorine in the bleaching process (8). In 1989 the Ontario petroleum refining industry was found to be a source of dioxins and furans during the regeneration of spent catalyst material used in the catalytic reforming process (9). Other sources were characterized in the late 1980's. These included automobile exhaust (10), metal recovery facilities (11), steel mills (12), and other metallurgical industries (13).

Enough is now known to suspect any combustion process as being a possible source of dioxins and furans. This was stated a decade ago by the Dow Chemical Company as the "Trace Chemistries of Fire" hypothesis (14). Little work has been performed on natural combustion sources such as forest fires, but a recent MOE study has shown that dioxins and furans are formed under forest fire conditions (15).

Dioxins and Furans as Multimedia Contaminants

All of the above studies show that humans can be exposed to dioxins and furans from air, water, and soil exposure pathways. A recent investigation showed that food commodities accounted for up to 95% of the exposure of Ontario residents to these chemicals (16). However, this exposure only amounted to 23% of the total tolerable daily intake (TDI) of 2,3,7,8-TCDD (Toxicity Equivalents or TEQ, see below) of 10 picograms (pg) per kg body weight (kg bw). All routes of exposure must be included in any model used to estimate exposure of humans to dioxins and furans. The multimedia exposure model used for Ontario has been described (17).

The basis for the multimedia approach is straightforward: once the maximum exposure level for a chemical has been determined, this quantity must be apportioned between all routes of exposure to protect human health. In this way, the combined exposure permitted by the separate guidelines would not exceed the TDI. Since food is the principal exposure pathway for Ontario residents, most of the tolerable daily dose would be apportioned to this pathway when determining guidelines. The net effect of the dose allocation exercise is that the guidelines set for any one exposure pathway will be much lower than if the entire daily tolerable dose was considered. The multimedia approach thus provides an effective means to protect human health, and in a sense symbolizes the interconnectedness of the ecosystem. The scientific advances in multimedia standard setting for the dioxins/furans can be applied to other environmental contaminants.

Challenges in the Analysis of Dioxins

The need for low detection limits. There are several reasons why parts-per-trillion (ppt) and parts-per-quadrillion (ppq) detection limits are required:

- ☐ the LD_{50} for 2,3,7,8-TCDD is about 1.0 μg/kg bw in the most sensitive species
- ☐ dioxins are hydrophobic and lipophilic, and consequently have high bioconcentration factors - therefore low detection limits are required to identify and track sources, especially in aquatic systems
- ☐ for the study of dioxin levels in human and animal tissues, sample sizes may be very small
- ☐ long-term chronic effects from low-level exposures are not well understood

The need to separate dioxins from other organics in the sample. This task is the most challenging and the success with which sample cleanup is performed will determine the detection limits, precision, and accuracy that are attained. Since dioxins may be present in the final sample extract at low picogram quantities, they may be "swamped out" by other organics that are present in quantities thousands of times greater. The sophisticated gas chromatograph-mass spectrometer (GC-MS) systems employed for the final separation and detection steps of the analysis, although highly selective, cannot achieve ppt and ppq detection limits unless presented with a "clean" sample in which virtually all other organics have been removed. It should also be remembered that highly contaminated samples where dioxin levels may be significant are precisely those samples where other chlorinated organic compounds - structurally similar to the dioxins and therefore potential interferences - are also likely to be present.

The need to separate the dioxins from each other. Of the 210 possible chlorinated dioxin/furan structures, only 17 are thought to be of toxicological significance. These are the ones with chlorine substitution at the 2,3,7 and 8-positions of the basic structure. The other "non-toxic" dioxins and furans are therefore interferences for the 17 "toxic" compounds. Schemes have been developed to relate the relative toxicity of each 2,3,7,8-substituted dioxin/furan with that of the most toxic: 2,3,7,8-TCDD. For example, octachlorodibenzo-p-dioxin (OCDD) is considered to be 1000 times less toxic than 2,3,7,8-TCDD, while 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-P_5CDF) is thought to be one-half as toxic. Therefore "toxicity equivalent", or TEQ factors can be applied to the concentrations of OCDD and 2,3,4,7,8-P_5CDF in a sample to determine their "2,3,7,8-TCDD-toxicity equivalent" concentrations. The OCDD concentration is multiplied by 0.001, while the 2,3,4,7,8-P_5CDF concentration is multiplied by 0.5. By doing this for all 17 of the 2,3,7,8-substituted dioxins/furans and then summing up the "2,3,7,8-TCDD-toxicity equivalent" concentrations, a total TEQ value is obtained that is very useful for regulatory and risk-assessment activities. However, this exercise is only effective if the "toxic" and "non-toxic" dioxins/furans can be separated from each other. Since the 210 dioxins/furans are so similar in structure to each other, this is not an easy task.

Dioxin Analysis State-of-the-Art

The challenges described above, although substantial, have largely been solved. High resolution GC-MS systems are available that can routinely detect 100 femtograms or less of 2,3,7,8-TCDD. Detection of 10 fg has been reported. Complex cleanup schemes have been developed that effectively isolate the dioxins/furans from potential chemical interferences in the most difficult sample types. The keys to successful cleanup are the number of separation steps employed, and the care and skill provided by the analyst. By using a series of gas chromatographic columns, and/or a combination of gas chromatography and high performance liquid chromatography, definitive separation of all 2,3,7,8-substituted dioxins and furans from all non-toxic dioxins/furans is possible.

Detection limits in real samples of ppt or better have been reported in samples of biota (including food) and soils; parts-per-quadrillion levels are routinely attained in 1L water samples; and detection of 0.01 pg/m^3 dioxin in ambient air is commonplace for the best 10-20 laboratories world-wide. A precision of 20-30% relative standard deviation (%RSD) for such work is possible if conditions and calibration standards are carefully controlled. However, it is not unusual to observe RSDs of 50-100% for dioxin in difficult samples when measurements are made near the method detection limit.

Where Do We Go From Here?

In a recent NATO survey, over 100 laboratories world-wide were identified that have some level of dioxin capability. Just 15 years ago, only about a dozen could make this claim. Of course, not all of these laboratories have the same level of expertise. There are probably no more than 20 labs who can boast state-of-the-art capability for isomer-specific determination of the 17 toxic dioxins/furans in virtually any matrix at ppt to ppq concentrations. One thing that even the top labs have not been able to do is to reduce the cost of analysis. It is still such a specialized area requiring highly trained staff and sophisticated, expensive instrumentation that private labs charge from $1,000 to $2,000 per analysis. Reduced cost for dioxin determinations would allow many more determinations to be performed. This would not only benefit environmental surveys (more locations monitored) and quality control (more replicates and round-robins), but would help multimedia investigations that are very sample-intensive (because all exposure pathways must be investigated).

Some researchers feel that some PCBs exhibit sufficient toxicity that they should be included with the 17 toxic dioxins/furans for the calculation of total TEQs. To do this would require even lower detection limits for the dioxins and furans. Since PCBs in sufficient concentrations are serious interferences for dioxin determinations, including some of them in the TEQ calculation would present a difficult challenge.

In the past 20 years, our knowledge of the formation, transport and fate, effects, and remediation of toxic environmental contaminants have greatly advanced because of dioxin/furan research. These advances would not have been possible without the parallel development of sophisticated analytical methodologies.

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THE MULTIMEDIA APPROACH AND POLLUTION PREVENTION: WHAT DO WE KNOW? WHAT DO WE NEED TO KNOW?

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ABSTRACT

The theme of this conference is "The Multi-media Approach: Integrated Environmental Protection" and the theme of this session is "Environmental Management Options". This paper places these themes in the broader context of the economic literature, to reviews the implications of that literature for the conference themes, and considers directions for future economic research. Special emphasis will be placed on the potential role of experimental economics in evaluating environmental policy.

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THE MULTIMEDIA APPROACH AND POLLUTION PREVENTION: WHAT DO WE KNOW? WHAT DO WE NEED TO KNOW?

OUTLINE

This paper places the concept of Integrated Environmental Protection into the economic literature, reviews the implications of that literature for the environmental management, and considers directions for future economic research. Special emphasis will be placed on the potential role of experimental economics in evaluating environmental policy.

I Introduction

The theme of this conference is "The Multi-media Approach: Integrated Environmental Protection" and the theme of this session is "Environmental Management Options". This paper is intended to place these themes in the broader context of the economic literature, to review the implications of that literature for the conference themes, and to consider directions for future economic research. Special emphasis will be placed on the potential role of experimental economics in evaluating environmental policy.

It will be useful to define our terms. Environmental Management Options are institutions governing the interaction between the economy and the environment. On the one hand we can attempt to prescribe the exact conditions and quantities in which industrial, municipal and domestic wastes can be discharged to the natural environment. This is the "command-and-control" option often denounced in the economic literature. On the other hand we can attempt to manipulate the information people have and the incentives they face so as to encourage them to change their interactions with the natural environment. This is the so called "incentive based" option frequently advocated in the economics literature. Of course we could attempt some mixture of these somewhat opposing approaches. I shall have a considerable amount to say about this choice in the middle section of this paper.

The terms "multi-media approach", "integrated environmental protection", and "pollution prevention" are somewhat vaguer. In practice, it seems we are using a multi-media approach if we recognize that any waste discharged to any one medium (for example toxic wastes discharged to the air during incineration) may eventually wind up in a second medium (water, for example) and possibly reincorporated into human activity through even a third medium, such as the fish we eat. We are not using a multi-media approach if we speak about air, water, or soil pollution by itself. Thus calling for a multi-media approach to environmental protection is effectively a claim that exclusive focus on any one of air, land or water is going to lead to important errors in public policy.

"Integrated environmental protection", it would appear to me, has essentially the same content. I take it that our environment is protected in an integrated manner if we simultaneously control discharges to air, water and land. "Pollution Prevention", on the other hand, seems to refer more to the choice between "end-of-pipe treatment" of residuals and process innovations designed to reduce residual discharges.

II Multi-media Approaches in the Context of the Economic Literature

Stressing integrated environmental protection is consistent with a large body of literature in environmental economics. Two strands in the literature seem particularly relevant. These are the materials balance approach to environmental economics and the rapidly expanding literature on economics of sustainable development.

A The Materials Balance Approach

The materials balance approach dates back to Kneese and forms the introductory portion of all environmental texts. The relationship between the economy and the natural environment can be pictured in various ways. The natural environment contributed physical materials and intangible services to the human economy. The economy discharges wastes to the natural environment where they may affect the original flow of materials and services. All materials extracted from the environment are ultimately returned to it as residuals. Focus on this fact immediately leads to the problem of multi-media contamination, since the control of discharges to any one medium must necessarily alter discharges to another.

Recycling and pollution prevention can reduce the residual load placed on the environment, but they have labour, capital and natural resource requirements themselves. We must select the appropriate level of recycling and pollution prevention, while recognizing that reduced demands on the environment may have an opportunity cost is terms of reduced incomes and consumption of other goods.

B The Economics of Sustainable Development

There is a large and growing literature on the economics of sustainable development. Much progress has been made in giving economic content to the idea of sustainable development. Here I wish to argue that efficiency should be a central concern of environmental quality management, and that it is too often neglected. In discussing policies for sustainable development, the literature also makes useful distinctions among general policies with environmental effects, framework policies concerning the environment, and issues surrounding project evaluation.

1 Sustainable Development and Efficiency

The literature distinguishes development from economic growth. Economic growth involves increases in measured income such as GNP. Development refers to indicators of human welfare. It is argued that growth cannot be sustainable, but that development can.

2 Policies for Sustainable Development

Stimulating work on environmental policy has occurred at all three levels. At the level of general policies, new developments in National Accounting are leading to the incorporation of depreciation of the Natural environment into the national accounts. At the level of environmental policy, the great debate concerns the choice between command-and-control regulation and incentive based regulation. Discussion of this is postponed to the next section. At the level of project evaluation, sensible suggestions have been made for the incorporation of environmental concerns, but general practice in the field lags far behind.

III The Choice of Regulatory Regime

This section focuses on the choice between Command and Control and incentive based regulation. The paradox is the great enthusiasm evidenced for market based schemes in the Green Plan and elsewhere while the assessments of the US market based schemes are surprisingly pessimistic. Several explanations for the limited success of these schemes are examined.

We may react to the presence of environmental problems in several ways: we may ignore them, we may try to solve them through the private law system, or we may try to regulate. In the last case we are faced with the choice between command and control and incentive based regulation. The case for incentive based regulation seems strong: incentive based regulations should minimize the cost of attaining any given level of environmental control and should provide strong incentives for the development of new control technologies. But the experience in the United States, especially with air emissions trading, has been only a modest success. Far fewer trades are made than had been expected. Explanations offered include excessive restrictions on trades (levels, sequential trades, the need to meet standards at every point (see Merrivell, Atkinson and Tietenberg), and political difficulties in getting the concept accepted. This last literature suggests concerns about the income distributional consequences of emission trading schemes is important.

IV The Contribution of Experimental Economics

This section suggests that some of the difficulties encountered in promoting and testing the ideas of incentive based regulation can be answered by laboratory experiments. Economics is not usually considered to be an experimental science. There is a growing literature, however, that tests the effectiveness of economic institutions in a laboratory setting. The systematic examination of institutions for allocating environmental rights is only beginning. There are, however, a number of experiments that show great promise. Further work in this area is advocated.

V Conclusion

This paper has attempted to place the themes of environmental management options and the multi-media approach to pollution prevention into the context of the economic literature. It has argued that great progress has been made in suggestions for incorporating environmental concerns into economic decisions, but that practice lies well behind theory. The debate between command-and-control and incentive-based regulation is unresolved. The newly developing field of experimental economics shows substantial promise in helping us to understand the nature of the debate.

D3 Costs and Benefits of Improved Environmental Control - Some Case Histories at INCO; W.C. Ferguson, INCO Limited, Toronto, Ontario

PAPER NOT AVAILABLE AT TIME OF PRINT

F2 A Consumer Perspective to Waste Prevention and Reduction; R. Lotzkar, Environmentally Sound Packaging Coalition and Consumers' Association of Canada, Vancouver, British Columbia

PAPER NOT AVAILABLE AT TIME OF PRINT

G7 Close Encounters of the Immune Kind: Antibody-Based Tests for Environmental Chemicals; B. Ferguson, ImmunoSystems Inc., Scarborough, Maine, U.S.A.

PAPER NOT AVAILABLE AT TIME OF PRINT

VOLUME I

SESSION A

ENVIRONMENTAL TRANSPORT AND FATE

VERBAL PRESENTATIONS

A2

CO_2 PRODUCTION AND CARBON CYCLING IN PRECAMBRIAN SHIELD WATERSHEDS

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INTRODUCTION

Concern about increasing atmospheric CO_2 concentrations has stimulated research on carbon cycling in natural systems. Northern temperate forest watersheds cover a large part of northern Ontario and Canada and have recently become the focus of intensive research regarding nutrient cycling. To understand the effect of anthropogenic influences, such as acidification and climate change, on their carbon cycle, the magnitude and pathways of carbon fluxes in these ecosystems must be evaluated. Generation of alkalinity which neutralizes acidic precipitation is also a part of the natural carbon cycle in watersheds.

Most of the carbon cycling studies in aquatic ecosystems have been conducted using a DIC and POC mass balance approach (see Wetzel, 1975, Ch. 17 for review). The studies of Herczeg (1985) and Quay et al (1986) are good examples of the potential of carbon isotopes to quantify lake carbon fluxes and determine major sources and sinks for carbon in systems of high productivity. Carbon isotopes have not been used in watershed-scale carbon and carbon isotope mass balances or to examine process controlling CO_2 cycling in northern temperate forests and lakes of lower productivity of the Precambrian Shield in Canada.

OBJECTIVES

The overall objective of our research is to evaluate the carbon fluxes between the main carbon pools, atmospheric and soil CO_2, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC), involved in the carbon cycle of these forested watersheds (Fig. 1). Our research is comprised of two main aspects. a) The role of soil CO_2 production in carbon fluxes and the generation of acid-neutralizing capacity in a terrestrial subcatchment and b) carbon mass and carbon isotope balances in the lake watershed. These whole lake mass balances will then be used to estimate : a) The net CO_2 flux from surface water to the atmosphere and the net conversion of inorganic carbon to organic carbon in the epilimnion; b) The conversion of organic carbon to DIC and DIC input from sediment porewaters in the hypolimnion zone and; c) The importance of the DOC and POC conversion to DIC in the lake DIC budget.

APPROACH

Our research approach involves the use of isotopic (^{13}C, ^{14}C) and chemical tools to evaluate the carbon cycling in forested watersheds in the Precambrian Shield. Isotopic fractionation during carbon transfer among the different carbon pools makes it possible to use carbon isotopes as natural tracers to evaluate sources and sinks of carbon and transfer rates between and residence times in the various carbon pools.

STUDY SITES

The study sites, Harp and Plastic Lakes, are located in the District of Muskoka, Ontario (Figure 2). These two lakes with differing physical characteristics were selected as end members by the Dorset Research Centre of the Ontario Ministry of the Environment and are being monitored as part of the Acid Precipitation in Ontario Study (APIOS) in the Precambrian Shield (Dillon et al, 1978., Scheider et al., 1979). Information regarding the size, type of forest and composition of the overburden and bedrock of Harp and Plastic Lake watersheds can be found in Jeffries and Snyder, 1983 and Girard and Snyder, 1985.

SAMPLING ACTIVITIES

Field activities have focussed on the evaluation of the main carbon pools involved in carbon cycling at Harp Lake and Plastic Lake watershed. The carbon pools that are being evaluated in these watersheds are soil organic matter, soil CO_2, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate organic carbon (POC) and sediment organic matter (SOM) (Fig.1). In general, sampling is being carried out on a monthly basis but is conducted twice a month during the summer.

Sampling of groundwater, soil organic matter and soil CO_2 has been carried out in Harp 4, a subcachment area of Harp lake watershed (Fig. 1). This well instrumented area has been the focus of extensive hydrological and geochemical studies (e.g Seip et al,1985; Dankevy et al., 1990).

Groundwater samples have been collected in wells installed in the upper (recharge areas), middle and lower part of the basin (discharge areas). A network of gas probes was installed to collect soil CO_2 samples. Stream sampling has been carried out at the weirs installed by the Dorset Research Center to evaluate stream discharge into Harp Lake and Plastic Lake. The lake sampling is conducted in the deepest part of the lake and includes a detailed stratified sampling of the epilimnion and hypolimnion waters.

Soil samples were collected in Harp 4-21 subcatchment area to be used in laboratory leaching experiments as part of the research concerned with the evaluation of carbon sources of dissolved organic carbon in groundwater.

The main parameters that are being measured are PCO_2, temperature, pH, DIC, DOC, POC and alkalinity. ^{13}C and ^{14}C analyses are performed on soil CO_2, DIC, DOC and POC samples. The ^{13}C analyses were done at the Environmental Isotope Laboratory, University of Waterloo by Mass Spectrometry and ^{14}C analyses were carried out at Lawrence Livermore National Laboratory by Tandem Accelerator Mass Spectrometry. The ^{13}C analyses are reported using the δ notation defined as

$$\delta^{13}C = [(R_{sample}/R_{standard}) - 1] * 1000 \text{ o/oo}$$

where R is the $^{13}C/^{12}C$ ratio in the sample and international standard PDB, respectively. ^{14}C results are expressed in percent modern carbon (pmc) relative to 95 % of the activity of oxalic acid standard in 1950 and normalized to a $\delta^{13}C$ of -25 o/oo PDB (Stuiver and Polach, 1977). Typical analytical errors are ± 0.2 o/oo and ± 1.0 pmc for ^{13}C and ^{14}C respectively.

SUMMARY OF RESULTS

This section summarizes the main results obtained to date in Harp Lake watershed focussing on the data concerning soil CO_2, and DIC in groundwater, streams and lake water. More detailed information about DOC, DIC and soil organic carbon cycling in Harp Lake catchment areas can be found in Schiff et al, 1990; Aravena et al, 1991 and Trumbore et al, 1991.

Soil CO_2

Soil CO_2 concentration profiles collected from spring 1990 (May) to the end of winter 1991 (March), show three distinct patterns. First, an increase in CO_2 concentration that reaches a maximum (1.2 o/o) at the end of the summer. Secondly, a decrease in CO_2 concentration occurs between July to December reaching a minimum concentration of 0.3 o/o and finally a slight increase from 0.3 o/o to 0.5 o/o is observed during the period December to March 1991. During this last period, the area was covered by at least 100 cm of snow.

The soil CO_2 concentration profiles at Harp Lake are explained by changes in rates of production and losses due to diffusion to the atmosphere.

The average $\delta^{13}C$ value for the soil CO_2 during the summer is around -22 o/oo shifting to -25 o/oo during the winter. This pattern is a reflection of the isotopic composition of the soil

CO_2 sources and changes in isotopic fractionation due to changes in rates of diffusion (Aravena et al, 1991).

Groundwater

The carbon isotopic composition of the groundwater DIC at Harp Lake watershed is a reflection of the chemical reactions that control the production of DIC in the unsaturated zone and in the aquifer sediments. In general, the ^{13}C composition of the groundwater is very similar throughout the basin, ranging from -22 o/oo to -24 o/o. This is a clear indication that the main process responsible for the generation of DIC (alkalinity) in this subcatchment is weathering of silicates. Dissolution of carbonate to produce DIC would result in $\delta^{13}C$ values for DIC of -12 o/oo to -18 o/oo.

The ^{14}C data in groundwater is in agreement with the ^{13}C scenario. All the wells closer to the recharge areas have ^{14}C values between 116 to 118 pmc. These values are close to the atmospheric CO_2 during 1990 (Schiff et al., 1990). Lower ^{14}C activities (112 pmc) are observed in groundwater DIC in the discharge areas suggesting a DIC contribution from groundwater depleted in ^{14}C. A depleted groundwater component has been identified as originating in the bedrock (^{14}C = 92 pmc) (Aravena et al, 1991).

Streams

The stream water shows the same carbon isotopic composition as the groundwater. This pattern implies the input of recent groundwater to stream flow generation. The presence of older carbon is also evident at Harp 4 stream, and could be associated with the input of beaverpond water and/or the discharge of ^{14}C depleted groundwater to the stream bed in areas close to the weir.

Lake water

Changes in carbon isotopic composition and concentration of DIC in a lake water column are linked to the main processes that control the production and consumption of DIC in lake environments.

$\delta^{13}C$ DIC profiles in Harp lake in 1990 (Fig.3) show a significant change in $\delta^{13}C$ values from -20 o/oo to -8 o/oo in the epilimnitic waters from spring overturn to late summer. This isotopic pattern could be associated with photosynthesis and/or isotopic exchange with atmospheric CO_2. During photosynthesis, phytoplankton preferentially use the lighter carbon isotope (^{12}C) as a carbon source, leaving the residual DIC enriched in the heavy carbon isotope. Isotopic exchange with atmospheric CO_2 will change the ^{13}C DIC signature in the same direction as photosynthesis. Since epilimnitic waters at Harp Lake are continuously oversaturated with respect to CO_2 and thus a continuous source of CO_2 to the atmospheric CO_2 (P. Dillon, M.O.E, unpublished data), isotopic exchange between lake DIC and atmospheric CO_2 should be a minor process. Preliminary ^{14}C data of lake DIC also support this statement.

The hypolimnetic ^{13}C DIC show an opposite isotopic trend to the epilimnitic DIC. A change to more depleted $\delta^{13}C$ values from -20 o/o to almost -26 o/oo is observed toward the fall. This isotopic shift must be due to oxidation of organic matter falling through the water column or resting on surficial hypolimnetic sediments. The average $\delta^{13}C$ value for particulate organic carbon (POC) is in the order of -28 o/oo. However, although there is an input of DIC from sediment pore water to the hypolimnion DIC, preliminary measurements of DIC in surficial hypolimnetic sediment pore water, yield a $\delta^{13}C$ of -22 o/oo, too heavy to account for shift in hypolimnetic DIC to -26 o/oo.

The effect of biological activity in the carbon cycling of the lake can also be observed in depth distributions of DIC concentration and pH. For the period spring overturn to fall, these profiles show a decrease in DIC concentration in the epilimnetic water and an increase in DIC concentration in the hypolimnetic water (Fig 4). These patterns result from the redistribution of CO_2 (aq) in the water column due to photosynthesis in the epilimnion and remineralization in the hypolimnetic water and sediments. pH data show an increase in pH in the epilimnion water from spring overturn toward the fall. The opposite is observed in the hypolimnion water. Hypolimnetic pH decreased during the same period. The changes in pH distribution are caused mainly by the same processes that change the DIC concentration, redistribution of CO_2 (aq) in the lake due to photosynthesis and remineralization of organic matter.

With regard to DOC cycling in groundwater, streams and lake water, further data collected in this project have confirmed and clarified some of the main findings reported by Schiff et al, 1990 about DOC cycling in Harp Lake watershed. These can be summarized as follows : a) Cycling of a significant portion of DOC in natural watersheds occurs on a short timescale (less than 40 years); b) The input of recent DOC to streams from saturated areas close to the stream bed explains the high ^{14}C values observed in stream water compared to groundwater. Groundwater is the main contributor to streams discharge in these watersheds and is characterized by low DOC concentration and the presence of older organic carbon; c) The older organic carbon present in the groundwater seems to be linked to carbon accumulated in the B soil horizon (Trumbore et al, 1991).

Field activities in this project will be finished at the end of 1991. Future activities will focus on the completion of isotope and chemical analyses to evaluate carbon mass and carbon isotope balances in the lake watershed. Once information including stream discharge rate on a monthly basis is available for the study period, these whole lake mass balances will then be used to estimate a) The net CO_2 flux from surface water to the atmosphere and the net conversion of inorganic carbon to organic carbon in the epilimnion; b) The conversion of organic carbon to DIC and DIC input from sediment porewaters in the hypolimnion zone and; c) The importance of the DOC and POC conversion to DIC in the lake DIC budget. A final report for this project is expected at the middle of 1992.

ACKNOWLEDGMENTS

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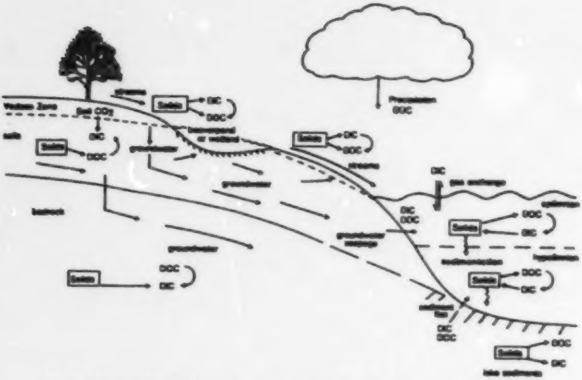
Vadose Zone
Soil CO2
soils
Solids
DIC
DOC
streams
beaverpond or wetland
groundwater
bedrock
Precipitation DOC
gas exchange
epilimnion
hypolimnion
sedimentation
groundwater seepage
sediment flux
lake sediments

Fig. 1. Carbon cycle in a watershed that does not contain carbonate minerals. DIC is dissolved inorganic carbon and DOC is dissolved organic carbon. The process DIC → DOC is referred to as carbon fixation and the process DOC → DIC is referred to as mineralization or decomposition.

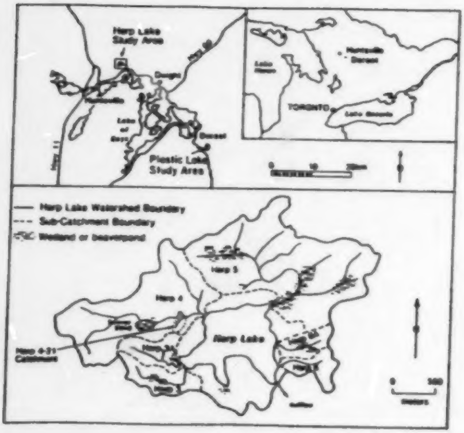
Harp Lake Study Area
Dwight
Huntsville
Lake of Bays
Dorset
Plastic Lake Study Area
Lake Huron
Huntsville
Dorset
TORONTO
Lake Ontario
0
10
20km
Harp Lake Watershed Boundary
Sub-Catchment Boundary
Wetland or beaverpond
Harp 5
Harp 4
Harp Lake
Harp 4-21 Catchment
Harp 3A
Harp 6
Outflow
0
300
meters

Figure 2. Location map of study areas.

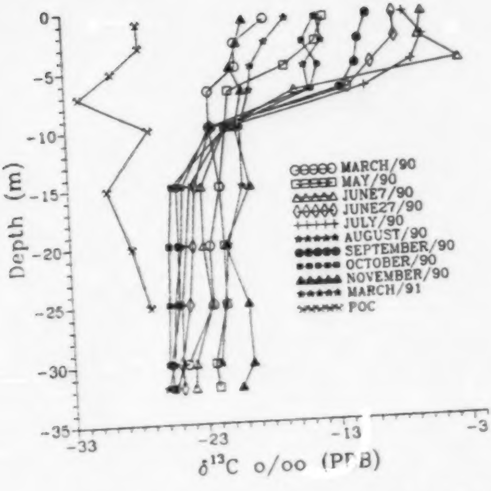

Fig 3. δ^{13}C DIC profiles, Harp Lake, 1990.

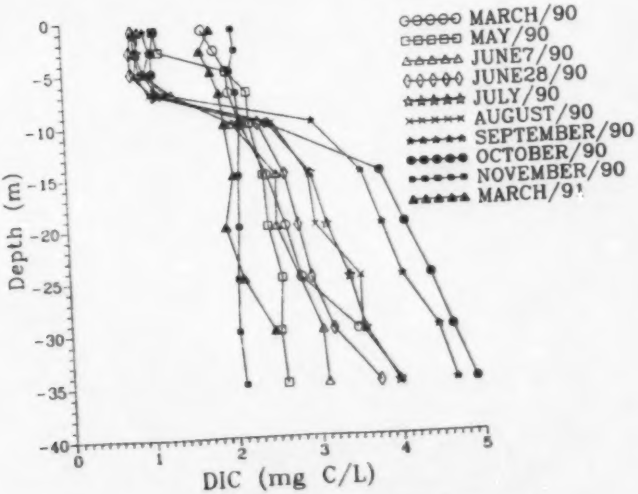

Fig 4. DIC concentration profiles, Harp Lake, 1990.

A3

ATMOSPHERIC CHEMISTRY AT THE DORSET SITE

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INTRODUCTION

The Eulerian Model Evaluation Field Study (EMEFS) was designed to provide sufficient data to allow a full evaluation of computer models of the atmosphere over Northeastern North America. The major thrust was in the evaluation of the two state-of-the-science Eulerian models being used to simulate and study the chemistry of acid deposition and oxidant formation. They are the Acid Deposition and Oxidants Model (ADOM) (Venkatram et al. 1988), supported by the Ministry of the Environment, the Atmospheric Environment Service of Environment Canada, the Electric Power Research Institute (EPRI), and Umweltbundesamt (West Germany) and The Regional Acid Deposition Model (RADM) (Chang et al. 1987) supported by the Environmental Protection Agency (EPA). These models include our current best understanding of the sources of gases to the atmosphere, the best available three dimensional meteorology, the most complete gas and aqueous phase chemistry available, and our best measurements of trace gas concentrations. Realizing the importance of the predictions of these models, it was deemed necessary to establish their credibility by comparison with data collected during EMEFS.

The Canadian component of the field study involved data collection from the MOE-APIOS and AES-CAPMoN networks. In addition, two sites were designated as intensive or enhanced sites. These were the AES site at Egbert (near Barrie) and the Ministry site at Dorset. The purpose of these sites was to obtain data using enhanced techniques that required operation by specially trained personnel or at a frequency not possible under normal operating conditions.

While the field study was put in place for model evaluation it became clear that the data obtained, especially that from the enhanced sites, could also be used to address a number of additional issues. The Canadian Institute for Research in Atmospheric Chemistry (CIRAC) took the lead in the co-ordination of the Canadian Air Chemistry Experiment (CACE) which aimed to ensure the collection of a complete data set capable of addressing some specific atmospheric chemistry questions. The work performed under this grant had as its focus the EMEFS program, but we were always mindful of the objectives of CACE.

We undertook a measurement program, at the Ministry site at Dorset, to measure the concentrations of a number of key species in the atmospheric oxidation cycle. Field measurement programs, each of six weeks duration, were undertaken in the summer of 1988, the summer of 1989 and the spring of 1990. In this paper we compare the data obtained for three periods during the 1989 and 1990 field campaigns, to show the type of information that can be gained on chemistry occurring at the measurement site when high quality, species specific trace gas concentrations are available.

MEASUREMENTS

The following is a listing of the chemical species that were measured at the Dorset site, and a brief description of the techniques used.

Hydrogen Peroxide and Formaldehyde using a Tunable Diode Laser Absorption Spectrometer (Schiff et al. 1983, 1987, Harris et al 1990, and Slemr et al. 1986)

NO and NO_y using an in-house fabricated, high sensitivity chemiluminescent NO analyzer similar to that used by Misanchuk et al. (1987). This was equipped with a gold converter for NO_y measurements (Fahey et al. 1986).

Ozone using a commercial UV absorption ozone analyzer (Dasibi Model 1003-AH).

PAN by GC/ECD as described by Blanchard et al. (1990).

NO_2 and NO_x using two modified commercial luminol NO_2 analyzers (Unisearch/Scintrex LMA-3) to measure NO_2 directly and NO_x (NO + NO_2) by use of a CrO_3 converter (Drummond et al. 1990).

Solar radiation using a U.V. radiometer (Eppley Labs 280-320nm).

Basic meterological parameters using a commercial meteorological system (MetOne) for wind speed, wind direction, temperature and humidity.

Boundary layer heights up to 500 meters were obtained by Ontario Hydro using an acoustic sounder.

RESULTS

We have selected three periods for consideration in this paper. These were selected on the basis of the maximum daily ozone concentrations to allow us to examine what we believe to be differing chemical environments. The first period was a summer period of relatively low ozone, July 22-25 1989. The second was a similar period but in the "early" spring, April 2-5 1990. The third was a period of much higher ozone from later in the spring, April 25-28 1990. We have deliberately chosen these periods to focus our interest on processes occurring outside the notable regional ozone episodes described in previous Technology Transfer Conference proceedings.

Ozone

The ozone data from the three periods are presented in Fig 1a-c. The diurnal variations in 1a and 1c are due to the presence of strong nocturnal inversions as has been discussed in Hastie et al. (1991), and will not be examined in further detail here. Of importance are the daytime concentrations as they are typical of the boundary layer concentrations. For the summer period, the daytime maxima were generally below 50 ppbv suggesting only moderate photochemical activity. Previous measurements, at this site, have shown ozone maxima in excess of 100 ppbv are common under regional scale ozone episodes. The early spring period shows an almost constant concentration of 40-45 ppbv which is currently believed to be typical of clean conditions. The period at the end of April showed daily maxima above 70 ppbv suggesting the existence of a major ozone source. It is important to note that for all three periods there was little diurnal variation outside that driven by the nocturnal inversion. In particular, there is little indication of an early afternoon ozone concentration maximum as would be expected in the presence of substantial local photochemical activity; thus we appear to be dealing with air masses lacking strong photochemical oxidant production.

Hydrogen Peroxide

The hydrogen peroxide data for these three periods are shown in Fig 2a-c. The most obvious feature is the absence of any hydrogen peroxide in the early part of April (Fig 2b). The diode laser instrument was working well with a detection limit below 250 pptv but no hydrogen peroxide was observed. In contrast, concentrations approaching 1 ppbv were observed later in the month (Fig 2c) and concentrations over 2 ppbv were observed in the summer (Fig 2a).

Formaldehyde

The formaldehyde behaved in a similar fashion to hydrogen peroxide. The early spring data (Fig 3b) show a low concentration scattered around the detection limit of 500 pptv. The data from later in the month were generally above 1 ppbv in the daytime with excursions up to 2.5 ppbv. The summer data show a good deal of scatter but average around 3 ppbv.

PAN

The PAN in early April was amongst the lowest measured at this site, and the extended period of concentrations below 175 pptv was less than the 5 year mean value for April as reported by Shepson and So (1991). The data from later in the month showed daytime maxima up to 500 pptv but the summer data were consistently lower, never exceeding 200pptv.

DISCUSSION

Consideration of all these data lead to a picture of the relative reactivity of the air masses.

For the early April data, the almost constant ozone concentration would normally be construed as meaning little photochemical oxidation. The low formaldehyde and PAN concentrations and the lack of a discernable diurnal variations support this interpretation, as any photochemically driven hydrocarbon oxidation would yield formaldehyde and likely PAN. The hydrogen peroxide concentrations appear to further support this conclusion. Hydrogen peroxide has been shown to be removed at humidities above 70% (Hastie et al. 1991) so the data for the first part of this peiod is not conclusive. However, the lack of a hydrogen peroxide response to the rapid drop in relative humidity on April 5 points to the lack of photochemical production as a likely explanation for the low concentrations . Thus, there is multiple species evidence for a lack of photochemical activity in this early part of April.

The ozone data for the summer period again shows little evidence for net photochemical production. However, the more reactive species point towards at least some photochemical activity. The hydrogen peroxide, PAN and formaldehyde data are all at elevated levels compared to the early spring data and give some indication of an afternoon maximum, particularly on July 24.

The later spring data presents somewhat more of a puzzle. The ozone levels are the highest of the three periods. The low hydrogen peroxide and formaldehyde concentrations, compared to the summer, and the lack of an afternoon maximum in ozone show there is less local photochemical ozone production than in the summer. However the hydrogen peroxide goes through a clear daytime maximum, and there is a rapid morning decay in formaldehyde suggesting an appreciable radical concentration. The back trajectories for this period originate in the source regions of the U.S. and pass over Southern Ontario so we are likely seeing an aged polluted air mass. Thus the low reactive species concentrations could indicate a small amount of local photochemical activity and the high ozone could simply be due to transport of the high concentrations generated in the source regions. The situation is complicated by the observations of Hoff (private communication 1991) that, during this period, there were intrusions of stratospheric air that brought high ozone concentrations close to the surface at Egbert, some 100 km from Dorset. We do not have the ability to track such events but would expect that if we were seeing the influence of a stratospheric intrusion then the higher ozone concentrations would be observed along with dryer air. Figure 5 is a plot of ozone against relative humidity for the entire 6 week measurement period. The daytime data from this period, April 25-28 is plotted as the filled squares and they cluster at high ozone and low relative humidity supporting the stratospheric influence. Clearly this is a very complex situation and we are currently attempting to better understand the situation through the application of a photochemical model.

CONCLUSIONS

We examined the concentrations of a number of trace gases at Dorset, during three 4-day periods of the EMEFS study. These periods were selected to be outside the major oxidant episodes to give further information on the chemistry occurring at this site. The summer period showed relatively low ozone concentrations, for the time of year, but the appreciable hydrogen peroxide and formaldehyde concentrations pointed towards some photochemical activity. In the early part of the spring the daytime ozone concentrations were similar to those in the summer but the hydrogen peroxide, formaldehyde and PAN concentrations suggest almost no photochemical activity. The late spring period had very high ozone concentrations, compared to the other periods, but the other species concentrations point to a very low level of photochemical activity. This could be due to the age of the airmass but may also be influenced by the intrusion of stratospheric air.

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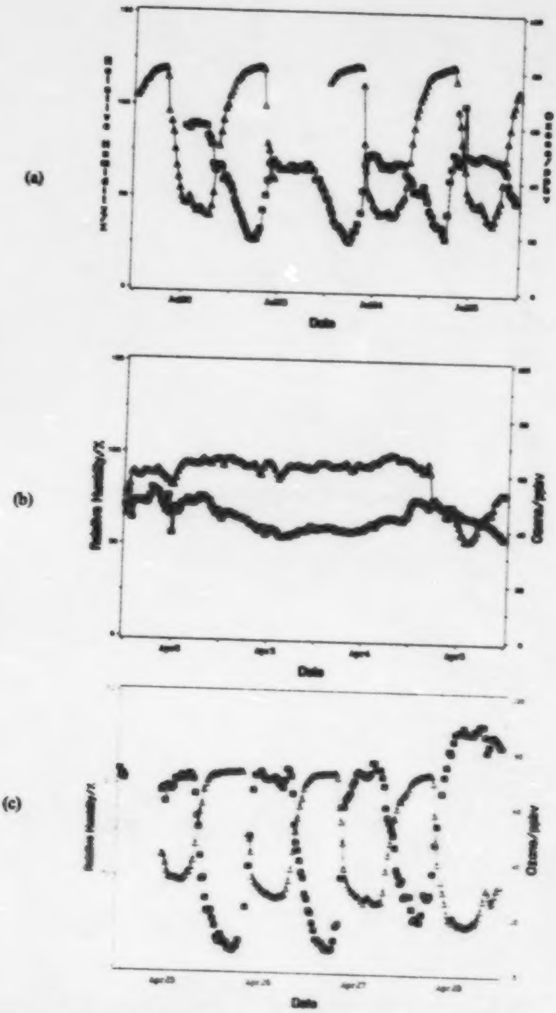

Figure 1. Ozone (squares) and Relative Humidity (triangles) for the periods (a) July 22-25 1989, (b) April 2-5 1990, and (c) April 25-28 1990.

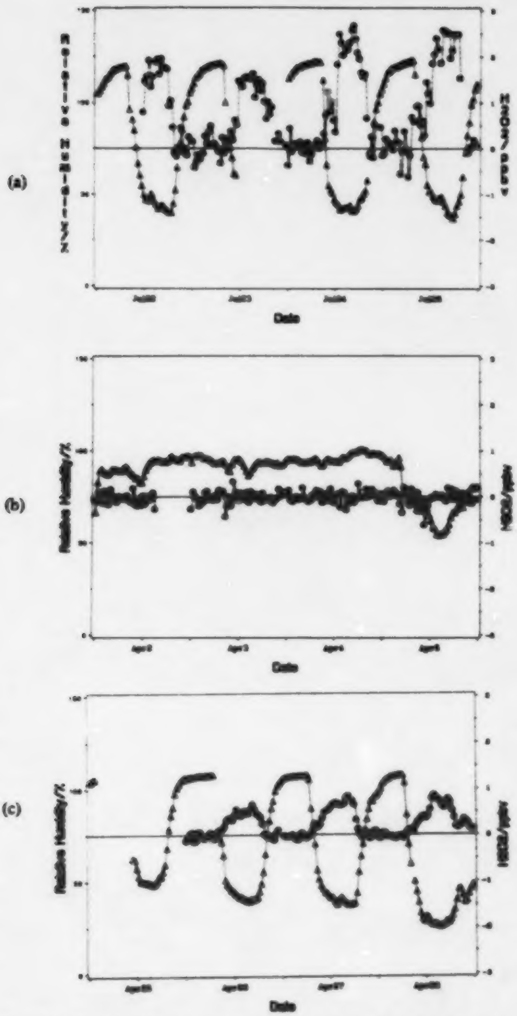

Figure 2. Hydrogen Peroxide (circles) and Relative Humidity (triangles) for the periods (a) July 22-25 1989, (b) April 2-5 and (c) April 25-28 1990.

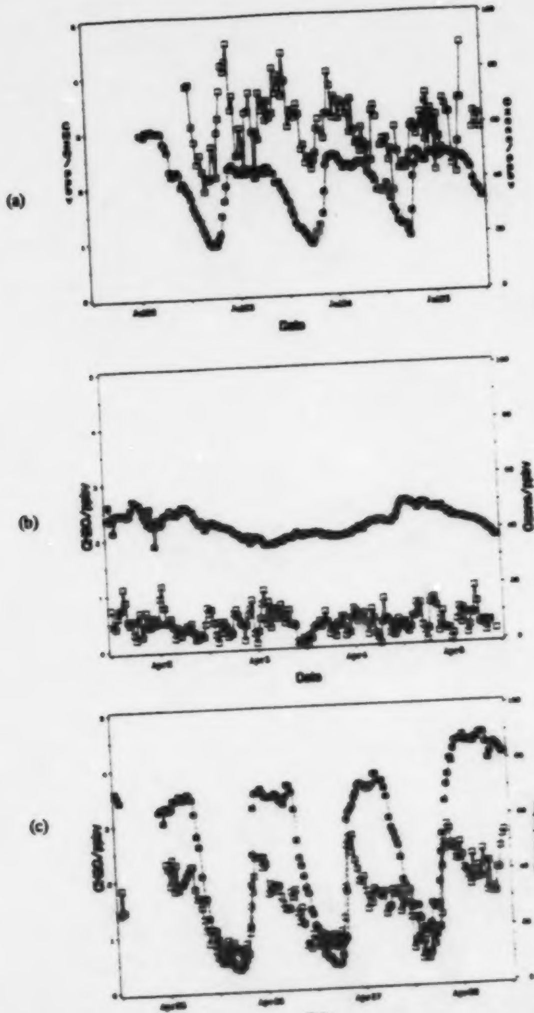

Figure 3. Formaldehyde (open squares) and Ozone (filled squares) for the periods (a) July 22-25 1989, (b) April 2-5 1990, and (c) April 25-28 1990.

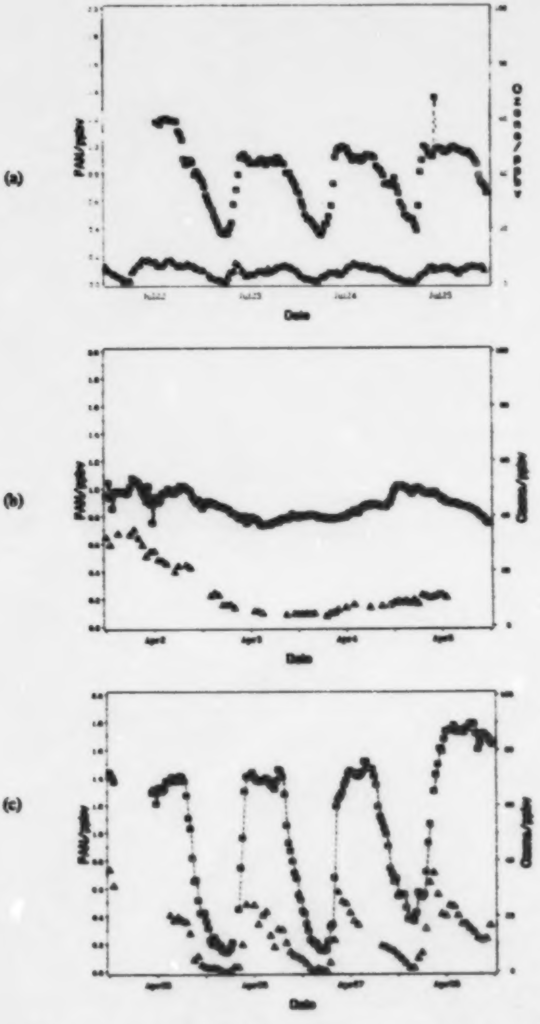

Figure 4. PAN (triangles) and Ozone (squares) for the periods (a) July 22-25 1989, (b) April 2-5 1990, and (c) April 25-28 1990.

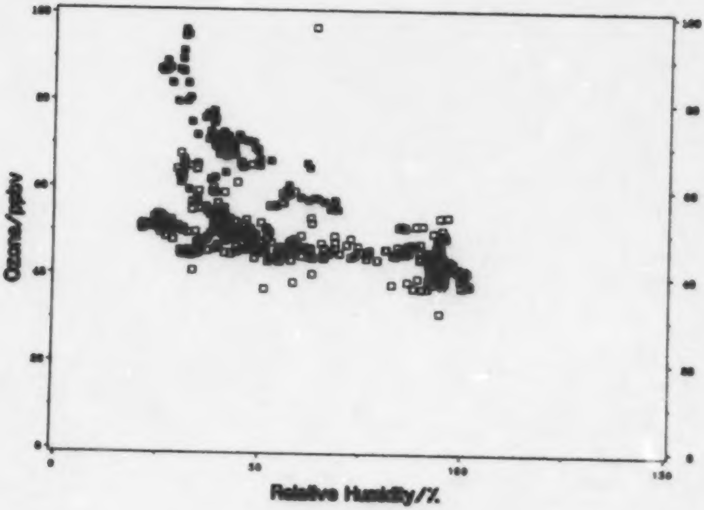

Figure 5. Daytime Ozone as a function of Relative Humidity for the period March 15 to April 30 1990. The data from April 25 to 28 are indicated by the filled squares, the remaining days by the open squares.

A4

THE DEVELOPMENT OF A LONG RANGE TRANSPORT MODEL WITH A NESTED FINE RESOLUTION GRID

by

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1. INTRODUCTION

Two existing numerical models, GESIMA, a mesoscale, non-hydrostatic meteorological model developed at the GKSS Forschungszentrum in Geesthacht, Germany and the long range transport Acid Deposition and Oxidant Model (ADOM) have been enhanced, adapted and interfaced to obtain a nested modelling system for the simulation of the transport, chemical transformation and deposition of a wide range of atmospheric pollutants.

The system described here is best suited to simulate the distribution of pollutants with a horizontal resolution of 5 to 20 km. A test run of the system for the Toronto area was carried out in a domain of 340 x 340 km with horizontal resolution of 20 km. A new series of simulations, with the same resolution, is currently being performed in a domain of 700 x 500 km covering most of Southern Ontario.

The resolution and the size of the domain place this system in the mesoscale, i.e. between the urban scale air quality models and the large scale models of long range transport of atmospheric pollutants (LRTAP). A mesoscale modelling capability is necessary to address the urban NOx/VOC issue if an understanding and eventual controlling of the precursor emissions is to be achieved. This approach is also required and to quantify the subgrid scale variability of pollutant concentrations simulated by the LRTAP models.

The modelling system developed in this study involves the interrelation of three main parts: the large scale ADOM, GESIMA, and the mesoscale version of ADOM. The programs interfacing these three parts are also an important part of the system. The interactions between these system components are schematically represented in Figure 1.

The original large scale version of ADOM uses meteorological fields generated by the Canadian Meteorological Centre (CMC) spectral diagnostic model. The mesoscale ADOM requires three-dimensional fields of meteorological parameters like horizontal and vertical wind velocity, temperature, humidity, turbulent diffusion parameters etc., with much finer horizontal resolution. Such fields are provided in this project by GESIMA. The role of the large scale ADOM, is to provide the initial and boundary conditions for the mesoscale simulations.

For a brief description of the main features of the system components, see Niewiadomski (1990). More details can be found in the original papers on ADOM (Scire et al., 1986; Venkatram et al., 1988) and GESIMA (Kapitza, 1987; Kapitza and Eppel, 1987; Jacob et al., 1990 and Mengelkamp, 1991).

2. THE NESTING SCHEME

For simulations periods longer than, say, one day, a mesoscale model must receive information of the development of the modelled fields outside its domain. This is achieved by "nesting" the mesoscale model inside an outer model operating in a much larger domain but with a more coarse resolution. In the system described here the outer model for GESIMA is the CMC diagnostic model, which also provides the meteorological fields for the large scale ADOM. The mesoscale ADOM is nested in the large scale version operating on the same grid as the CMC model.

In this system the mesoscale domain covers a specified number of cells of the large scale grid. The large scale data from these cells, and those adjacent to the mesoscale domain, can be interpolated in space and, if necessary, in time and then passed to the mesoscale model.

The mesoscale ADOM receives information from the outer model through time dependent boundary conditions. Similar time dependent boundary conditions are used for some parameters in GESIMA, but for the main fields (wind, temperature and humidity) a technique of the Newtonian relaxation or "nudging" is used.

The concept of nudging (Hoke and Anthes, 1976; Stauffer and Seaman, 1990; Seaman and Cole, 1991) involves the introduction of additional, artificial tendency terms to the prognostic equations, which force the solution of the mesoscale model toward the observed, or modelled, large scale conditions. This approach is used to combine the fine scale variability with the large scale tendencies which cannot be simulated by the mesoscale model itself, and seems to be more efficient and reasonable than introducing those tendencies by means of the time dependent boundary conditions alone.

These artificial tendencies - the nudging terms, applied at each time step, are proportional to the difference between the values of large scale field at given grid point (interpolated from the results of the outer model) and the actual solution of the mesoscale model. The coefficient of proportionality - the nudging coefficient, can be a function of height and has values of the order of 0.0001/sec.

Note that the described above nesting scheme represents so called one-way nesting, i.e. the results of the mesoscale simulations do not influence the large scale models. This allows all components of the system to be run separately and to simulate several emission/pollution scenarios using the same meteorological fields.

3. SIMULATION OF THE HIGH OZONE EPISODE (August 1 - 4, 1988)

This section gives the details of a test run of the system. The episode for this study, August 1 - 4, 1988 was chosen because of the high ozone concentrations observed at that time in Southern Ontario, and the availability of the results of the large scale ADOM simulation and the observational data.

Some results of this simulation concerning the time evolution of the ozone concentrations in Toronto and its areal distribution in the whole domain are presented and discussed in Section 4.

The large scale ADOM is routinely run on a 33 x 33 grid based on a polar stereographic projection with nominal horizontal resolution of 127 km (true at 60° N). That domain covers most of eastern North America. The same grid is used in the CMC spectal model.

In this simulation, the 'nested' grid of GESIMA and mesoscale ADOM covers 9 cells of the large grid, including the Toronto cell and the 8 cells around it. Thus, the mesoscale domain extends over an area of about 120,000 km^2 with Metropolitan Toronto area located about 25 km south of its centre. The domain is divided into 17 x 17 mesoscale cells resulting in a horizontal resolution of about 20 km.

The basic vertical structure of the large scale ADOM, with 12 variable depth layers has been retained for the mesoscale version of the model. The same structure was adopted for the GESIMA simulations. The tops of the ADOM layers are located at 56.2, 135.8, 250.7, 416.3, 655.3, 1000.0, 1497.2, 2214.5, 3249.2, 4741.6, 6894.5, and 10000.0 metres above the ground level. The vertical resolution of the upper layers of ADOM is too coarse for GESIMA, and therefore the 4 top layers of ADOM were split into two layers. In effect, 16 rather than 12 vertical layers are used in GESIMA. The GESIMA/ADOM interface averages the data from those split layers before using them in appropriate layers of ADOM.

GESIMA was run for a period of 96 hours starting on August 1, 1988 at 00:00 GMT (July 31, 20:00 EDT) and a time step of 45 sec was used throughout this period.

The large scale ADOM was not run under this project. The output files, from a previous simulation for the same period were used. These files together with the output of GESIMA, were processed by the interfacing programs and provided the input data for the mesoscale ADOM simulations.

Since the mesoscale ADOM requires GESIMA output data, the ADOM run started one hour later then that of GESIMA, at 01:00 GMT, on August 1, 1988 and continued for 95 hours.

4. RESULTS

The time evolution of the ozone concentration in the Toronto cell of the mesoscale model is compared with observations in Figure 2.

The times of maximum and minimum modelled concentrations coincide with those observed at the surface in Toronto (except for a secondary peak in observed concentrations during the early morning of Aug 4 which is not reflected in the model results).

The values of the modelled ozone concentrations are also in fairly good agreement with the observed ones, although the model does not predict the highest measured concentrations (e.g. 112 ppb observed in Toronto on Aug. 2 at 14:00 EDT versus 68 ppb modelled). These discrepancies can be partly attributed to a significant area and depth represented by an ADOM cell, compared to the point measurements. Comparisons made for several other locations with available surface measurements of ozone concentrations yielded similar results.

Examples of the areal distribution of ozone and nitrogen oxides are shown in Figure 3. While the NO_x distribution is dominated by strong area and point source emissions in the Toronto area and the ozone is distributed more evenly, both fields display a pronounced horizontal variability impossible to simulate with a large scale - coarse resolution models.

5. CONCLUSIONS

A mesoscale modelling system for transport, chemical transformation and deposition of atmospheric pollutants has been designed, programmed and tested in one case study over Southern Ontario.

The system is capable of simulating the distribution of various air pollutants with a spatial resolution of 20 km or less. It can detect local effects in this scale that are impossible to simulate with large scale models like the original version of ADOM.

A preliminary analysis of the simulation of the early August 1988 high ozone episode over Southern Ontario, showed reasonably good agreement of the model results with observations.

A case study of the same episode using a slightly modified model, over a large domain covering most of Southern Ontario is currently underway.

6. ACKNOWLEDGEMENTS

The author would like to thank Drs. P.K. Misra and C. Fung of the Ontario Ministry of the Environment, Dr. D. Eppel of GKSS, and Mr. L. Shenfeld of The MEP Company for their assistance in this study.

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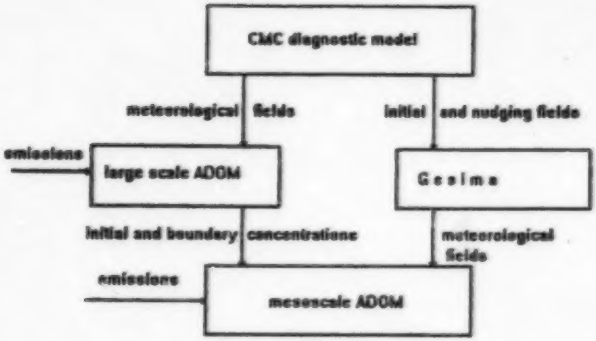
CMC diagnostic model
meteorological fields
initial and nudging fields
emissions
large scale ADOM
Gesima
initial and boundary concentrations
meteorological fields
emissions
mesoscale ADOM

FIGURE 1

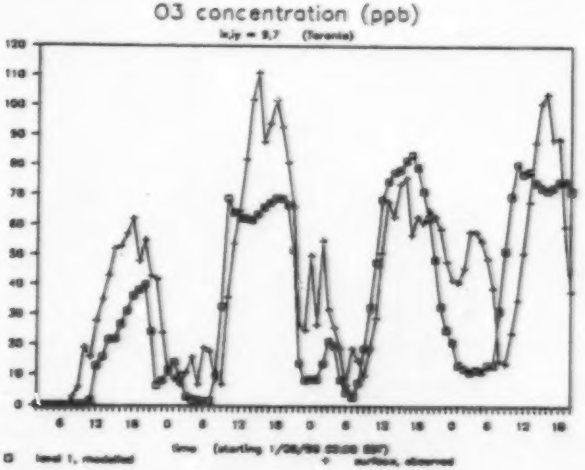

FIGURE 2

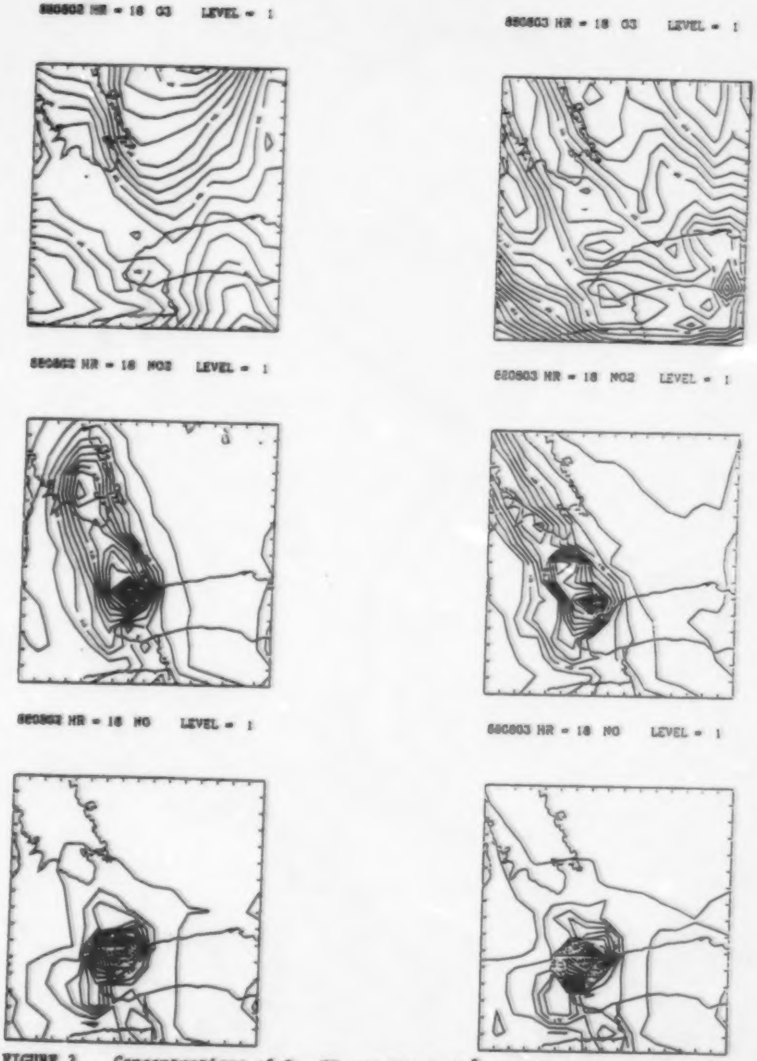
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FIGURE 3. Concentrations of O_3, NO and NO_2 ($\mu g/m^3$) in the lowest layer of the model at 2 p.m. EDT (18:00 GMT) on the second and third day of simulation.

A6

Modelling Concentration Fluctuations in the Atmosphere

by

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1 INTRODUCTION

The concentration of a contaminant at a fixed point in a plume in the atmosphere is highly variable, with a mean deviation comparable to the time average, and peaks reaching a factor of five or more times the average. A typical time trace of concentration is shown in Figure 1. Here, c is instantaneous concentration, $\bar{c}$ is a time average over period T, c' is the instantaneous deviation from the average. The plume can be highly intermittent, i.e., concentration may drop to zero for short time periods during the total period T. An intermittency factor (γ) is typically used for describing the fraction of time non-zero concentration are present at the measurement point.

A knowledge of the magnitude and frequency of the peaks is essential from a regulatory point of view if avoidance of significant occurrence of nuisance odours is desired. The same type of information is also required for emergency planning purposes for releases of toxic gases.

To predict probability of peak exposures, a modelling system is required to estimate the magnitude and frequency of concentration fluctuations under a variety of meteorological conditions and for different source types.

MODEL

A modelling system for concentration fluctuations consists of three (3) basic components:

1) a module to estimate time-averaged concentrations at receptor points of interest,

2) a module to estimate plume intermittency and time-averaged concentration fluctuation intensity at that receptor,

3) a model to estimate the shape of the frequency distribution of fluctuations that make up the time-averaged fluctuation intensity.

In the model presently under development, the first module consists of a computer model developed by Concord based on the OME Clean Air Program (CAP) GAS model to predict one hour average concentrations. The second module consists of an empirical Gaussian model to provide plume intermittency (γ) and time-averaged intensity ($i^2 = \overline{c'^2} / \bar{c}^2$). The intermittency and intensity are used in the third module which estimates the magnitude and frequency of concentration fluctuation using a log-normal distribution.

The OME GAS model is described in detail in OME (1990) and will not be addressed here further.

2 CONCENTRATION FLUCTUATION MODEL DEVELOPMENT

Concentration fluctuations are a result of two physically distinct atmospheric processes. The first is related to small scale turbulent mixing and the second to large scale atmospheric motions. The two processes can be superimposed onto each other to describe the atmospheric process of dispersion.

Small scale mixing occurs within a marked volume of fluid or plume. Parcels of fluid from various origins (contaminated and clean air) intermingle with each other to generate fluctuations in concentration at points relative to the centre of mass or centreline of the plume. These fluctuations are analogous to turbulent velocity or temperature fluctuations at a fixed location in an Eulerian frame of reference and are generally termed "in-plume" fluctuations.

The second process reflects the concentrations at a position which is fixed relative to the source. Here, fluctuations occur due to varying relative distance between plume-centerline and the fixed position. The plume is physically moved by the large scale motions of the atmosphere, commonly known as "meandering". Generally, the plume meandering component dominates the fluctuations from small sources at travel times less than one Lagrangian time scale ($t < T_L$) and the in-plume component dominates from broad sources at all times or from small sources at large travel times ($t >> T_L$).

The occurrence and distribution of zero concentrations at a receptor is determined by the large eddies while statistics of non-zero concentrations are determined by smaller eddies. While this connection is obviously not precise, it suggests that there might be more order in conditionally sampled statistics for which zero concentrations are ignored (roughly speaking, 'in-plume' statistics). Conversely, the intermittency should reflect variations due to the large-scale inhomogeneous features of the concentration field.

As the plume meanders, it will pass over a fixed receptor for only a fraction, γ, of the time. It is not the mean concentration c or its variance c'^2 that is important in determining the peak concentration but rather the mean $\overline{c}_p$ and variance that $\overline{c_p'^2}$ occurs when the plume is present over the receptor. These are called the "conditionally averaged", or "in-plume", mean and variance. Most plume dispersion models predict the unconditional mean $\overline{c}$ and not the conditional value $\overline{c}_p$. Fortunately, there is a relationship between unconditional and conditional statistics.

Defining $P(c)$ as the probability that the concentration $c(t)$ exceeds c and noting that a fraction, $1-\gamma$, of the time, the concentration at a receptor is zero, the cumulative distribution functions are coupled via,

$$\begin{aligned} P(c) &= \gamma\, P_p(c) \;;\; c \ge 0 \\ &= 1 \qquad\quad ;\; c < 0 \end{aligned} \qquad [1]$$

Further, the probability density function is p(c) = - dP(c)/dc, so

$$\begin{aligned} p(c) &= \gamma p_p(c) + (1-\gamma)\delta(c)\ (c \ge 0) \\ &= 0 \qquad\qquad\qquad\qquad (c < 0) \end{aligned} \qquad [2]$$

where the Dirac function is the result of the discontinuity in p(c) at the origin. The n-th concentration moment is defined as

$$\overline{c^n} = \int_0^\infty c^n p(c)\,dc \qquad [3]$$

and the unconditional and conditional n-th moments are related via,

$$\overline{c^n} = \gamma \overline{c_p^n}\,. \qquad [4]$$

Then the first central moments or means are coupled via

$$\bar{c} = \gamma \overline{c_p}\,. \qquad [5]$$

Defining fluctuating components as,

$$\begin{aligned} c' &= c - \bar{c} \qquad c \ge 0\,, \\ c_p' &= c - \overline{c_p} \qquad c > 0\,, \end{aligned} \qquad [6]$$

and it can be shown that the variances and intensities are related via,

$$i^2 = \frac{i_p^2}{\gamma} + \frac{(1-\gamma)}{\gamma} \qquad [7a]$$

or

$$\gamma = \frac{i_p^2 + 1}{i^2 + 1} \qquad [7b]$$

where:

$$i^2 = \overline{c'^2}/\bar{c}^2 \ \text{and} \ i_p^2 = \overline{c'^2_p}/\bar{c}_p^2 \ . \qquad [8]$$

A concentration fluctuation model then consists of specification of at least two of i, i_p and γ to close the equation set for time-averaged first and second moments of the concentration distribution. Furthermore, to estimate the fraction of time that concentration peaks could present a problem, specification of the shape of the concentration probability limits function is required.

2.1 MODEL FOR TIME-AVERAGED CONCENTRATION INTENSITY AND INTERMITTENCY

The Gaussian formula forms the basis of the Empirical Gaussioan Model (EGM) developed by Wilson et al. (1982a, b) and Wilson (1982, 1986) to simulate concentration fluctuations from a continuous source. The model ideally is suited for in-plume fluctuations but does not directly deal with meandering.

The initial model proposed by Wilson et al. included a pair of point sources above and on either side of the plume axis which served as variance sources. This was done to account for the off-axis maximum in total variance production. Subsequently, Wilson and Simms (1985) revised this assumption to include a single variance point source above the plume axis. The following assumptions form the basis of the model:

1. The distribution of $\overline{c'^2}$ in the cross-wind and vertical is a result of diffusion alone (using the same diffusivity as per the mean concentration $\bar{c}$).

2. Crosswind and vertical profiles of the variance are self-similar and only a function of the downwind distance.

3. The variance originates from a point source above the plume centerline where most of c'^2 is observed to be produced due to the strong $\bar{c}$ gradients.

4. Surface dissipation of $\overline{c'^2}$ is approximated by an image sink with a strength equal to a fraction of the variance source.

5. The variance flux is not a conserved quantity like mass and decays with downwind distance due to dissipation by molecular diffusion. This "along-wind" dissipation is simulated from a balance between local advection and dissipation.

The Gaussian plume equation for $\overline{c'^2}$ is then

$$\overline{c'^2} = \left(\frac{q}{2\pi U\sigma_y\sigma_z}\right)^2 \left(\exp\left(1/2y^2/2\sigma_y^2\right)\right)$$

$$\left[\left(\exp\left(-\frac{(z-h_v)^2}{2\sigma_z^2}\right) - \alpha\exp\left(-\frac{(z+h_v)^2}{2\sigma_z^2}\right)\right)\right] \qquad [9]$$

where q is the variance source strength, α is the sink strength parameter and h_v is the variance source height given as

$$\left(\frac{h_v}{\sigma_z}\right)^2 = \left[\left(\frac{h}{\sigma_z}\right)^2 + \phi^2\right] \qquad [10]$$

where h is the height of the plume centerline and ϕ is a constant.

Wilson et al. (1982b) argue that the upward displacement of the variance source term, above the release height, is reasonable because the zone of maximum c'^2 production will drift upward as surface reflection flattens the mean concentration profile and reduces $\partial\bar{c}/\partial z$ near the ground.

The variance source strength (q) was developed from the conservation equation and wind-tunnel observations showing advection in balance with dissipation. Wilson et al. (1982b) show that the ratio of q to Q (mass emission rate) has a functional form

$$\frac{q}{Q} = \frac{C_2\lambda}{(\lambda^2 + \lambda_0^2)^{C_1/2}} \qquad [11a]$$

$$\lambda_o = \frac{C_3}{C_4\left(\frac{L_w}{d} + 1\right)} \qquad [11b]$$

$$\lambda = \sqrt{\sigma_z \sigma_y / H}\,. \qquad [11c]$$

where C_1, C_2, C_3, and C_4, are constants, d is the source diameter, H is the mixing layer depth and L_w is the average turbulent length scale felt by the plume.

The above formulation is reasonable since fluctuation levels are, intuitively, strongly dependent on the source size (laterally and vertically) and turbulent scale near the source and weakly dependent on source size further downwind.

The constants (α, ϕ, C_1, C_2, C_3 and C_4) were derived by Wilson via systematic to curve fitting wind tunnel to data of Fackrell and Robins (1982a, b).

Wilson (1986) has further specified a similar equation set for i_p, enabling us to complete the description of time-averaged first and second moments of the concentration distribution in the atmosphere for pollutants released from arbitrary sources.

2.2 MODEL FOR FREQUENCY DISTRIBUTION OF FLUCTUATIONS

The conditional and unconditional statistics are coupled via the intermittency factor but an appropriate probability density function (pdf) is required to determine the probablity of occurance of peak concentrations. A number of pdf's have been proposed and applied including the exponential, log-normal and clipped-normal.

The distincly different shapes of the pdf's for log-normal, exponential are shown schematically in Figure 2. The exponential function is physically realistic only for highly intermittent plumes which have a conditional fluctuation intensity of unity. While a log-normal has the capability of dealing with fluctuation intensities different from unity (non-intermittent), it has the physically unrealistic property that the probability of observing a concentration only slightly greater than zero, is very small, while at the same time there is a large probability of observing zero) concentration, when intermittency removes the plume from the receptor. In highly intermittent plumes where there is a significant probability of zero concentration, the exponential model realistically predicts a smooth monotonically increasing probability of observing small concentrations.

The log-normal distribution seems appropriate with the above equation set because the EGM is an in-plume fluctuation model which has been expanded to predict i_p and γ. It should be noted that the exponential distribution does not require the prediction of i_p since γ is a residual of the distribution.

3 EVALUATION OF GAS/EGM PREDICTIONS WITH FIELD DATA

The results of the GAS/EGM model are compared with the SF_6 stationary field measurements taken during 1989 (ERCB, 1990). The field tests were categorized under four atmospheric release scenarios, i.e.

i) Neutral stability surface release
ii) Stable stability surface release
iii) Neutral stability elevated release
iv) Stable stability elevated release

There was insufficient QA/QC'd data for the fourth data set but there is good quality data for the others.

The primary objective of these comparisons, is to evaluate the performance of the EGM module when coupled with the OME Clean Air Program GAS model. The GAS model calculates mixing height, plume rise, dispersion coefficients and mean concentrations. The EGM module calculated i, i_p and γ as well as the percentile values via the log-normal distribution.

The performance of the above is evaluated via standard statistical and graphical procedures. Considerable effort has been made to determine the appropriate performance measures for dispersion models (Hanna, 1988). A wide variety of indices have been suggested since it is difficult to arrive at a single quantitative index of accuracy.

Table 1 presents the typical source characteristics used in the model. Measured emission rates for each case was used in predicting the downwind concentration. The exit temperature was taken as the ambient air temperature resulting in momentum generated plume rise.

The EGM parameters (i, i_p and γ) as well as the log-normal distribution and the exponential distributions are compared against measured values.

In many cases, the SF_6 samplers were located well off the average wind vector direction which defines the centreline of the plume. This was primarily due to the wind changing direction during the measurement period. A significant portion of the data were taken at $y \geq 3\ \sigma_y$ where σ_y is predicted via the GAS model.

To provide a fair model evaluation data set, only measurement taken within $\pm 2.2\ \sigma_y$ were considered. This significantly reduced the number of available cases for evaluation. Table 2 presents a summary of the final valid data set used in the evaluation.

Table 3 summarizes the statistical performance measures for unconditional intensity (i), conditional intensity (i_p) and intermittency (γ) for the four scenarios. Insufficient data were available for assessing stable/elevated releases.

The following discussion is limited to surface releases under stable atmospheric conditions under which a majority of the data was acquired

3.1 UNCONDITIONAL INTENSITY

Unconditional intensity is calculated via the EGM module as described earlier. The EGM significantly overpredicts and has virtual zero index of agreement (I), for all cases.

The relative bias as a function of y/σ_y is presented in Figure 3. There is a significant trend with respect to crosswind distances. As discussed earlier, the unconditional intensity is unstable at the fringes (i.e., $y > 2\sigma_y$). This is very apparent from the figures where the predicted intensity is almost 3 orders of magnitude greater than the observed. The relative bias is significantly reduced at $y < 1.5\sigma_y$ for all cases which should be, therefore, the limit of applicability.

3.2 CONDITIONAL INTENSITY

In-plume or conditional intensity as predicted via the EGM is presented. The model seems to provide adequate representation of the conditional intensity. The conditional intensity is slightly overpredicted for stable conditions.

The errors as a function of y/σ_y are shown in Figure 4. The errors generally range between -0.75 to +0.25 for all scenarios, with the largest errors occurring for $y > 1.4\ \sigma_y$. The small deviations are due to I_p not being a function of y/σ_y.

3.3 INTERMITTENCY

There is significant scatter in the intermittency data shown little correlation. The error seem to be divided evenly between systematic and unsystematic for surface release scenarios but the error is mostly unsystematic for the elevated release (Table 3). In all scenarios considered, γ is underpredicted by approximately 50%.

The model tends to overpredict γ near the centreline and significantly underpredicts γ is the fringes are approached (Figure 5). This trend is expected since $\gamma \alpha 1/I^2$.

3.4 EVALUATION OF LOG-NORMAL AND EXPONENTIAL DISTRIBUTIONS

An evaluation of the log-normal and exponential distributions is presented. The log-normal is recommended by Wilson for the EGM. The evaluation compares the CDF's of both distributions against observed values. The predicted distributions use measured values of I_p, γ and the percentile to generate normalized concentrations which are compared to normalized (i.e., normalized by the measured mean) observed values.

The above comparison can be made independent of the EGM since the distribution of concentrations are invariant to crosswind location and EGM results. The CDF's are effectively isolated from previous calculations.

Table 4 summarizes the results of the statistical analysis. The exponential model is better performer for all scenarios.

The primary objective of the concentration fluctuation model is to calculate peak concentrations, thus the errors associated with percentile levels becomes significant.

Figure 6 presents the relative error (P-O/O) as a function of percentile, for percentiles greater than 75%-ile. The log-normal model, underpredicts concentrations for percentiles greater than

85%-ile by less than a factor of 2. The exponential model tends to overpredict at the higher end and underpredict at lower percentiles. The curves are similar for both models.

4 SUMMARY

The EGM is a poor predictor of i for crosswind distances greater than 1.2 σ_y. These poor predictions lead to poor predictions of γ as well. The model provides good estimates of i_p but generally underpredicts i_p. The largest errors are associated with i.

The log-normal distribution was not an adequate model for predicting peak concentrations. It tended to underpredict concentrations at higher percentiles. The exponential distribution provided the best estimate of the probability distribution. The exponential model is most applicable to highly intermittent plumes and a review of the conditional intensity shows that i_p is very close to unity and γ is approximately 0.5.

The applicability of the exponential model will likely be a function of atmospheric length scale, source diameter and elevation.

ACKNOWLEDGEMENTS

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Table 1

Source Characteristics

SOURCE CHARACTERISTICS		ELEVATED	GROUND
Height	(m)	2.3	0.3
Radius	(m)	0.0785	1.1
Exit Velocity	(m/s)	26.7	0.17
Exit Temperature	(°C)	Ambient	Ambient

Table 2

Summary of Evaluation Data Set

RELEASE SCENARIO	ATMOSPHERIC STABILITY	[illegible] (m)	[illegible]	NO. OF CASES	%	AVERAGE METEOROLOGICAL				
						u_* [illegible]	$\bar{u}$ [illegible]	[illegible]	L (m)	z_i[1] (m)
Elevated	Stable	1045	1.2	2	2	0	3.5	-7.0	0	105
	Neutral	1300	1.1	13	12	10.1	2.0	-2.5	95	246
Ground	Stable	700	1.0	82	77	21	5.0	-43	74	120
	Neutral	600	1.2	10	9	3	4.05	-1.0	290	330
				107	100%					

[1] Calculated as per CAP pre-processor.

Table 3

Summary of Statistical Indices for EGM Evaluation

	Unconditional Intensity		Conditional Intensity		Intermittency	
	O	P	O	P	O	P
Count	82	82	82	82	82	82
Avg	1.6	109.1	0.6	0.6	0.6	0.3
STD	1.1	301.7	0.3	0.1	0.3	0.3
Gross Error	107.7		0.2		0.4	
P/O	78.6		1.1		0.6	
(P-O)/O	72.6		0.1		-0.5	
RMSE	346.4		0.4		0.7	
Intercept	109.6		0.7		0.0	
Slope	-0.3		0.1		0.5	
R	0.0		0.3		0.4	
[illegible]	89%		16%		46%	
[illegible]	11%		84%		54%	
[illegible]	0.0		0.4		0.5	
MFE	-1.6		-0.1		1.0	

Table 4

Summary of Statistical Indices for Log-Normal and Exponential Distributions

		Log-Normal	Exponential
	Observed	Predicted	Predicted
Count	1944	1944	1944
Avg	0.1	1.5	0.2
STD	11.6	1.6	12.0
Gross Error		4.7	2.1
P/O		2.0	2.0
(P-O)/O		1.0	1.0
RMSE		8.7	8.8
Intercept		1.1	0.7
Slope		0.1	0.0
R		0.5	0.0
[illegible]		1%	97%
[illegible]		99%	3%
[illegible]		0.3	0.0
MFE		0.6	0.0

Figure 1

Typical Time Variation of Instantaneous Concentration of a Contaminant in a Plume

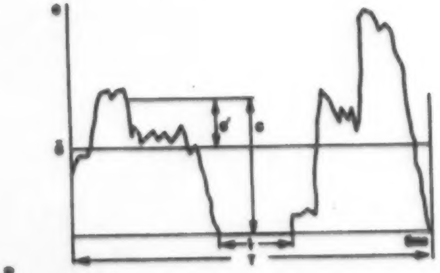


Figure 2

Log-Normal and Exponential PDF's

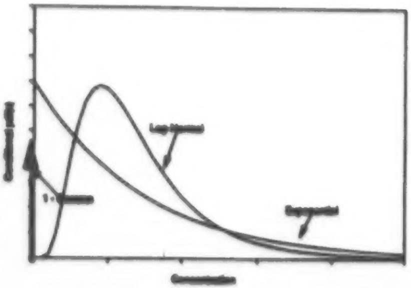


Figure 3

Relative Error of Unconditional Intensity (I) versus Normalized Crosswind Distance

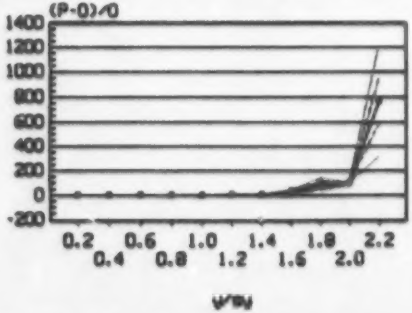


Figure 4

Relative Error of Conditional Intensity (I_p) versus Normalized Crosswind Distance

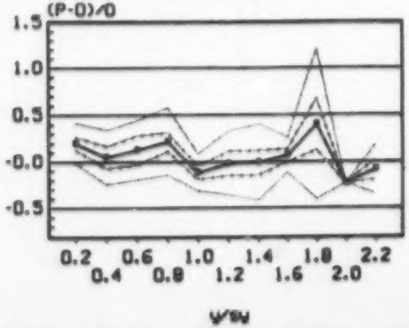


Figure 5

Relative Error of
Intermittency (γ) versus Normalized Crosswind Distance

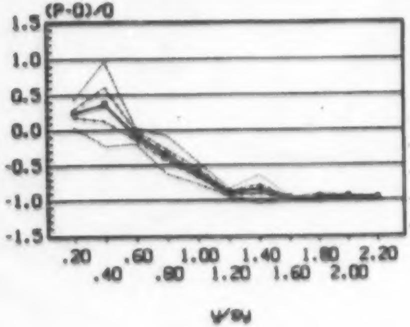


Figure 6a

Relative Error of
Log-Normal Percentile versus Percentile

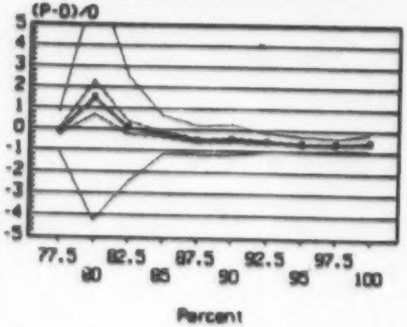
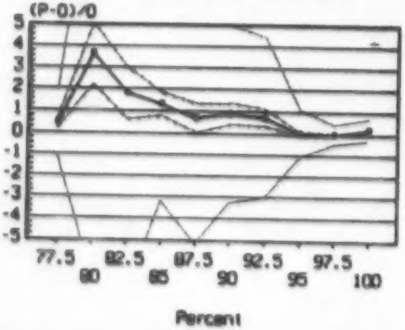


Figure 6b

Relative Error of
Exponential Percentile versus Percentile



A6

MEASUREMENTS OF NATURAL AND ANTHROPOGENIC VOLATILE ORGANIC COMPOUNDS IN THE REGIONAL ATMOSPHERE

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Introduction

The frequent occurrence of excessive ozone concentrations remains one of the more contentious Canadian atmospheric problems, particularly in the Province of Ontario. International, national and provincial decisions on control strategies for oxidant precursors are at present in various stages of formulation. For instance, the Federal/Provincial LRTRAP (Long Range Transport of Air Pollutants) Committee is developing a management plan for dealing with Canada's O_3 problem and meeting Canada's international obligations under the NO_x/VOC protocol [1]. However, as documented in a workshop report of the CIRAC-sponsored Canadian Oxidant Research Program (CORP), there remain numerous outstanding scientific issues concerning the relative importance of anthropogenic and natural VOC emissions and NOx vs VOC in controlling the formation of O_3 and other oxidants in urban and rural air [2].

Analysis of Canadian and U.S. data obtained to date, e.g. the Eulerian Model Evaluation Field Study (EMEFS 88), indicates the important role of natural VOC, particularly isoprene, in the atmospheric chemistry of forested rural areas [3-6]. Clearly, ambient distributions of individual hydrocarbon species are affected by a large number of complex factors, e.g. emission source distribution and strength, transport, and chemical transformation, which should be all treated properly in oxidant modelling. In this respect, it is particularly important to take into account the vast differences in their atmospheric lifetimes as well as abundance [7-9]. The present project is aimed at obtaining a more comprehensive database for natural and anthropogenic VOC both on a climatological and espisodic basis, as part of the CORP activities. For comparative purposes, distributions as well as absolute concentrations of various hydrocarbons (HC) in the C_2 to C_{10} range are being characterized at urban (York U. and downtown Toronto), rural (Dorset, Egbert, and Hastings) and remote (Fraserdale) sites in

Ontario. This paper highlights some of the key findings from the data obtained thus far at these sites.

METHODOLOGY DEVELOPMENT AND TESTING FOR HC MEASUREMENTS

The presently employed gas chromatography (GC)-based analysis of ambient HC involves several sample handling steps, i.e. (1) vacuum cleaning of stainless steel sampling canisters at 80-100 °C ; (2) air sample collection and storage in canisters at ca. 30 psi; (3) cryogenic (liq. Ar) sample preconcentration on glass beads; (4) cryogenic (liq. N_2) sample focusing onto the GC column head; and (5) GC separation and signal detection by flame ionization detector (FID). Although all the gas-handling system components are operational for routine analysis of air samples, they are continually being tested and improved to achieve an optimum performance. Some of the recent improvements include:

Step (1): A high vacuum compatible humidifier to treat the canisters with water vapor following the initial dry cleaning has been installed to passivate the canister wall surfaces. This canister-humidification procedure has been found crucial for maintaining the storage stability of standard reference hydrocarbon mixtures prepared in-house at ppb level.

Step (2): Sample stability during storage in canisters has been tested extensively using ambient air samples collected at several urban and rural sites. Generally speaking, while alkane and alkyne hydrocarbons were found to be stable over a period of a month, alkenes in some canisters exhibited significant increase followed by subsequent loss. These canisters which misbehaved have been identified as those used previously to collect highly polluted air. Thus, it is conceivable that their interior wall surfaces may have been contaminated by heavy hydrocarbons which could not be removed by vacuum cleaning. The observed increase in alkene concentrations may be attributable to surface catalyzed reactions (hydrolysis) of these contaminants. However, similar storage test for several canisters containing Toronto air has not so far exhibited any discernible gain or loss. Thus, the fractional increase in alkene concentrations during storage in contaminated canisters is expected to be more pronounced for relatively clean air samples. Thus, it was decided to dedicate some canisters for sampling relatively clean background air only.

Step (3): Humidity in the air samples collected in canisters must be removed in order to prevent GC column plugging and FID flame-out. Also, one of the columns in use, i.e. Al_2O_3/KCl PLOT, is highly sensitive to the presence of water in terms of stability of retention times of individual HC. The Nafion dryer has been found to be less than ideal because it traps heavier HCs as well as water. It also suffers from blank problems and causes isomerization of some olefins [10]. The most effective water trap found to date is a Teflon tubing (ca. 15 cm operated at canister pressure) cooled by dry ice. Stainless steel tubing was found to trap heavier

HC (>C_5) at a comparable temperature. These tests were conducted with standard HC mixtures prepared in-house at 1-10 ppbV level which represents typical concentrations in ambient air, and with ambient air samples collected in Toronto.

Step (4): An efficient coolant (Liq. N_2) handling system for the cryofocusing unit has been designed and constructed to prevent an excessive coolant consumption. The system has been functioning satisfactorily for over two years.

Step (5): Two different columns and dedicated GC instruments are currently being employed for the separate analysis of light and heavy HC, since a complete analysis of all the C_2-C_{10} HC using only a single column is difficult to accomplish. A narrow bore capillary column operated down to -50 °C has been performing well for the C_3-C_{10} range, but it consumes excessive amounts of coolant and is too expensive for us to operate on a routine basis. A relatively new type of column (Al_2O_3/KCl) operated at >30 °C for C_2-C_6 has been working reproducibly for over two years without severe column deteriorations presumably encountered by some groups. We have been also employing a wide-bore capillary column (SPD1-DB1; 90 m long) operated at above ambient temperatures without any water trap. This column has been performing satisfactorily for the analysis of the majority of C_3-C_{10}, including aromatics and mono-terpenes.

RESULTS OF THE DATA ANALYSIS

Grab samples have been collected at seven sites, representing urban (Toronto), rural (Dorset, Egbert, Hastings) and remote (Fraserdale) environments. The three sites in Toronto are York University campus on top of a four storey building, Queen's Park, and the CN tower at ground, 330 m and 440 m levels. Dorset is situated in a valley surrounded by trees, whereas Egbert and Hastings sites are on a hill top near the centre of a clearing. Fraserdale is in a boreal forest. More than twenty C2-C10 HC species have been quantitatively identified for air samples collected at all sites.

To illustrate the overall features of the spatial distribution of HC, site-to-site comparison of median values of representative species during the summer months is shown in a logarithmic scale in Figure 1. In this figure, the data from Fraserdale (alkane and alkene only, 1990-91), Dorset (88) , Egbert (88), and York U. (91) are selected because of the availability of sufficiently large data sets for statistical analysis. It can be noted that for the alkanes and aromatics, the concentration in urban air are generally a factor of 10 higher than those of the remote site at Fraserdale. As to be expected, the concentrations for the rural sites (Dorset and Egbert) are seen to be intermediate between urban and remote sites. The biogenic HC, isoprene, was the most abundant HC species at the two forested sites (Fraserdale and Dorset), and is also prominent at the other two sites shown in this figure. For the purpose of comparing atmospheric reactivity of various HC species, the HO oxidation rates ($k_{HO}[HC]_i$ at 298 K) are calculated from these median concentrations, as shown in Figure 2. Isoprene is seen to be the most dominant HC governing the local atmospheric chemistry at the remote and rural sites and is also a significant contributor at the York U site. Another notable feature in Figure 1 is the marked changes in the alkane distributions from site to site. Namely, in a remote site (Fraserdale) heavier and more reactive alkanes are greatly depleted probably because of the aging of air masses arriving at these sites as compared with those closer to urban sources of anthropogenic HC components. Comparisons of more detailed results on rural and urban HC distributions are presented below.

RURAL DATA: As part of the 1990 Spring EMEFS, an intensive episodic study was conducted at Dorset during the first week-long warm spring period (April 21 - 27) with relatively high O_3 concentrations for the purpose of examining the relative contribution of biogenic HC, isoprene, and anthropogenic HC to the local oxidant formation. The results are summarized in Table 1. In this table the removal rates of C_2-C_7 alkanes and alkenes by HO-radicals, i.e. $k_{HO}[HC]_i$, are given relative to that of n-butane. In this table the relative oxidation rates of the three most dominant HC species are indicated by the shaded boxes. It can be noted that the dominant HC contributors are all olefinic species and that isoprene is often the most dominant species. Thus, these results suggest that the biogenic HC, isoprene, is a highly important HC precursor of O_3 not only during the summer months but also in the warm spring period, consistent with the '88 Summer EMEFS data which indicated a strong temperature dependence of ambient concentrations of isoprene at this site [5,11].

During the summer months of 1991, an HC measurement intercomparison study has been conducted at Egbert by the AES and York U groups using, respectively, a packed column for C_2-C_5 HC and the two capillary GC systems described in the preceding section. A representative HC data thus obtained is shown in Figure 3. For all the compounds detected by more than one GC systems, agreement is seen to be excellent. It can also be noted that the biogenic HC, i.e. α- and β-pinenes as well as isoprene, are amongst the most abundant species. These results are generally consistent with those obtained at this site in 1988, except that α- and β-pinenes were not measured at that time [4].

HC concentration/time profiles and their relative concentration distributions at the several rural sites have been examined in detail to discern any observable trends and patterns indicative of source signatures and also to provide representative HC data corresponding to O_3 episodes as an input to the development of explicit chemical mechanism for oxidant modelling. Summarized in Table 2 are the values of rank correlation among various HC species from the Dorset (90) and Hastings (91) data using the Spearman method which is less sensitive to outliers than the more commonly used Pearson method. The shaded boxes contain values >0.8 which were arbitrarily chosen as a cut off point to indicate a high degree of correlation. The highest correlation coefficients are seen for C_4-C_6 alkanes at both sites. Good correlation is to be expected for alkanes regardless of the air mass history, since all these compounds are not only of anthropogenic origin but also of comparable atmospheric reactivity [7-9]. Similarly, poor correlation among the other HC species may be taken as evidence for the wider range of sources and history of air masses arriving at these rural sites.

TORONTO URBAN DATA: It became apparent to us that reliable information on HC distributions in the urban plume from the Toronto area is critically needed in order to better understand the Ontario rural HC data described above. The most extensive urban HC data obtained thus far by this group are at York U. campus, i.e. >3 samples daily during May to August 1991. Some limited HC measurements have also been carried out in downtown Toronto at OME Queen's Park air monitoring site and at the CN Tower. The CN Tower measurements were intended to observe the local source at the base level and also the long range transport of air mass originating from the south across Lake Ontario at elevated levels (330 and 450 m platform). These results are summarized below.

Table 3 shows the values of rank correlation among various HC species observed at York U. and the CN Tower base level. The York U data used for this analysis included all measurements made during the May to August period irrespective of wind directions and other meteorological conditions. A remarkably high degree of correlation can be noted in this table for both sites. As shown in Figures 4 and 5, a very similar pattern of HC distributions originating from local traffic and other urban sources was observed at both sites and also at the Queen's Park site. Although it remains to be seen whether these HC distributions reflect contributions from all the major emission sources in the Toronto area, they serve as a reference database for developing a suitable lumping scheme of HC and their chemical reactions to be incorporated in urban and regional oxidant modelling.

An illustration of striking differences observed for HC distributions as well as their absolute concentrations at the CN Tower base level and at a higher level (330 m) is given in Figure 6. These measurements were made in midafternoon with moderate breeze from the south over Lake Ontario. HC concentrations are seen to be generally lower by a factor of >2 at the 330 m level, but are markedly reduced for the highly reactive olefinic compounds such as 1-butene (a factor of 5.5), iso-butene (8.0), 1-pentene (10), and 1,3-butadiene (12). These observations are indicative of the long range transport and the corresponding aging of the air mass aloft. On the other hand, the HC distribution at the base level is similar to those observed at York U and at Queen's Park (cf. Figures 4 and 5), suggesting the local traffic as the primary source. Another notable feature in Figure 6 is the presence of significant concentration of isoprene at the base level where there is not much vegetation in the immediate vicinity. Conceivably, the observed isoprene may be of an anthropogenic origin. There appears to be no relevant literature information concerning combustion-related emission of isoprene as well as other highly reactive olefinic compounds. Figure 7 illustrates the HO radical oxidation rates of various HC species corresponding to the HC distribution data shown in Figure 4. The predominant role of isoprene in the local photochemistry at this downtown site is apparent from this figure.

CONCLUSION

Hydrocarbon compositions in the C_2-C_{10} range have been surveyed during the spring and summer months at one remote (Fraserdale), three rural (Dorset, Egbert, and Hastings), and three Toronto urban (York U., Queen's Park, and CN Tower) sites in Ontario. Isoprene, which may be of both biogenic and anthropogenic origin, was frequently one of the most abundant species at many of these sites including the Toronto urban sites, and was primarily responsible for the local formation of oxidants. Winter-time data in urban sites, which would not contain the biogenic contribution, may thus aid in resolving this question. A high degree of similarity have been observed among the relative abundance of various hydrocarbons observed particularly among the data obtained at urban sites. These data can be used as a reference database for the development of a chemical module for use in urban plume modelling. In addition, the data from the remote (Fraserdale) site and from the elevated levels at the CN tower reveal significant aging of the air masses arriving at these sites. Further temporary and spatially resolved data on both natural and anthropogenic hydrocarbons in representative Canadian rural and urban settings are required for an assessment of urban and regional oxidant problem.

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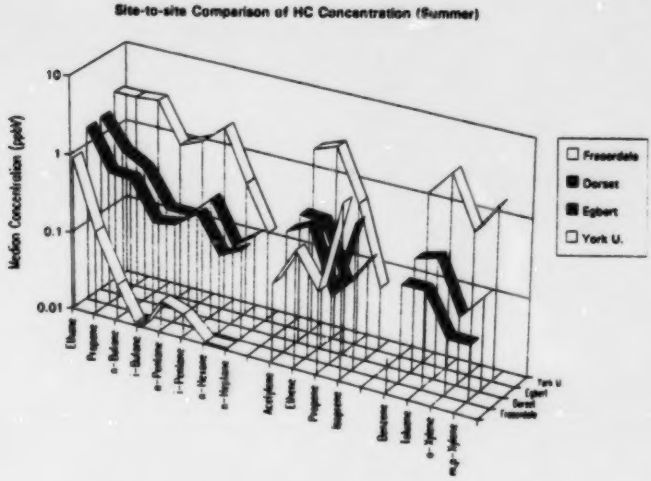

FIGURE 1

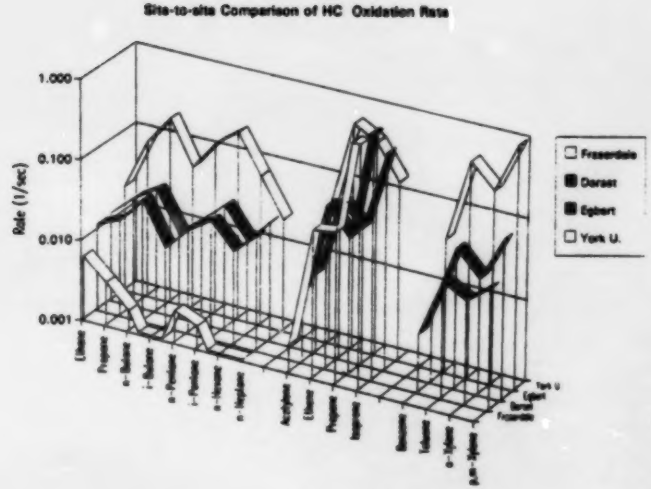

FIGURE 2

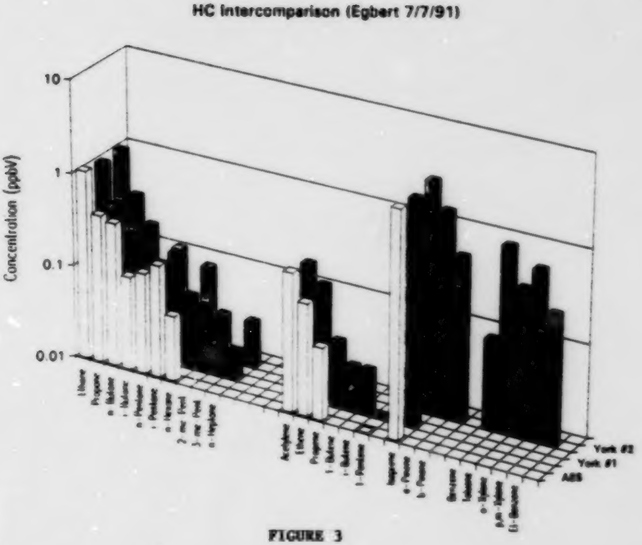

FIGURE 3

TABLE 1

Relative Oxidation Rates of Hydrocarbons at Dorset (1990 & 1988)

DATE(April)	21	23	24		25	26	27					1988
TIME	14:20	13:35	10:40	15:55	12:00	10:05	9:00	11:00	13:00	15:15	16:15	median #
TEMP (C)	12.8	22.9	20.5	23.0	26.0	25.0	20.7	26.3	26.4	26.3	28.0	
Ozone (ppbV)	44	54	45	95	71	71	51	65	73	71	75	
Alkyne & Alkene												
Acetylene	0.64	1.02	0.66	0.61	0.32	0.37	0.1	0.25	0.36	0.34	0.52	0.01
Ethylene	4.14	7.97	6.30	2.53	1.91	2.14	3.35	2.63	5.06	7.25	7.79	1.30
Propene	6.39	17.47	15.22	4.90	3.20	4.24	3.46	2.88	11.18	10.05	10.88	1.20
1-Butene	1.73	4.62	4.26	1.09	0.59	0.81	1.48	0.63	1.63	1.72	2.34	
iso-Butylene	11.30	60.71	15.19	9.59	5.29	8.28	14.82	4.10	16.48	7.88	17.36	
Isoprene	1.20	10.40	1.49	1.05	8.96	5.73	15.51	3.87	20.30	21.61	24.82	58.54
Alkane												
Ethane	0.63	1.24	0.73	0.48	0.38	0.43	0.29	0.30	0.51	0.48	0.75	0.17
Propane	1.15	1.52	1.15	0.86	0.68	0.72	0.51	0.67	0.95	0.75	0.99	0.30
n-Butane	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
iso-Butane	0.41	0.40	0.40	0.37	0.39	0.41	0.34	0.35	0.34	0.58	0.35	0.32
n-Pentane	0.43	0.39	0.49	0.43	0.52	0.46	0.70	0.63	0.49	0.34	0.58	0.58
iso-Pentane	0.71	0.48	0.87	0.78	0.86	0.81	1.10	0.98	0.77	0.55	0.73	0.88
n-Hexane	0.21	0.27	0.28	0.19	0.21	0.22	0.38	0.31	0.23	0.18	0.21	0.44
cyclo-Hexane	0.68	4.40	1.94	1.29	0.81	0.87	3.10	1.86	1.71	2.21	10.25	
n-Heptane	0.13	0.18	0.18	0.10	0.07	0.18	0.15	0.14	0.07	0.08	0.27	0.85

TABLE 2

Rank Correlation: Dorset (April, 90)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	ISOPREN
C2H2	1.00	-0.34	0.87	0.21	0.74	0.07	0.12	-0.10	-0.10	-0.02	0.03
C2H4	-0.34	1.00	-0.26	0.54	-0.02	-0.20	-0.18	-0.10	-0.10	-0.04	-0.30
C2H6	0.87	-0.23	1.00	0.11	0.61	0.28	0.36	0.16	0.16	0.28	0.28
C3H6	0.21	0.54	0.11	1.00	-0.01	-0.51	-0.46	-0.47	-0.47	-0.45	-0.65
C3H8	0.74	-0.02	0.61	-0.01	1.00	0.45	0.51	0.32	0.32	0.47	0.36
n-C4H10	0.07	-0.20	0.28	-0.51	0.45	1.00	0.96	0.93	0.93	0.92	0.69
i-C4H10	0.12	-0.18	0.36	-0.46	0.51	0.96	1.00	0.87	0.87	0.87	0.67
n-C5H12	-0.10	-0.10	0.16	-0.47	0.32	0.93	0.87	1.00	1.00	0.98	0.79
i-C5H12	-0.10	-0.10	-0.47	0.52	0.32	0.93	0.87	1.00	1.00	0.98	0.79
n-C6H14	-0.02	-0.04	0.28	-0.45	0.47	0.92	0.87	0.98	0.98	1.00	0.81
ISOPREN	0.03	-0.30	0.28	-0.65	0.36	0.69	0.67	0.79	0.79	0.81	1.00

Hastings (Jul - Aug, 91)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	ISOPREN
C2H2	1.00	0.60	0.38	0.35	0.31	0.64	0.50	0.44	0.48	0.49	0.34
C2H4	0.60	1.00	0.05	0.58	0.27	0.68	0.51	0.62	0.65	0.78	-0.07
C2H6	0.38	0.05	1.00	0.10	0.55	0.34	0.73	0.21	0.24	0.06	0.20
C3H6	0.35	0.58	0.10	1.00	0.03	0.26	0.27	0.12	0.12	0.12	-0.14
C3H8	0.31	0.27	0.55	0.03	1.00	0.31	0.55	0.14	0.12	0.13	0.54
n-C4H10	0.64	0.68	0.34	0.26	0.31	1.00	0.83	0.95	0.94	0.89	0.10
i-C4H10	0.50	0.51	0.73	0.27	0.55	0.83	1.00	0.74	0.75	0.63	0.06
n-C5H12	0.44	0.62	0.21	0.12	0.14	0.95	0.74	1.00	0.99	0.94	-0.04
i-C5H12	0.48	0.65	0.24	0.12	0.12	0.94	0.75	0.99	1.00	0.95	-0.07
n-C6H14	0.49	0.78	0.06	0.12	0.13	0.89	0.63	0.94	0.95	1.00	-0.10
ISOPREN	0.34	-0.07	0.20	-0.14	0.54	0.10	0.06	-0.04	-0.07	-0.10	1.00
BENZENE	0.68	0.76	0.53	0.72	0.57	0.52	0.66	0.35	0.37	0.38	0.17
TOLUENE	0.35	0.69	0.25	0.10	0.30	0.55	0.48	0.59	0.62	0.72	-0.29
o-XYL	0.28	0.65	-0.08	0.72	-0.02	0.04	0.01	0.01	0.04	0.16	-0.33
m,p-XYL	0.01	0.15	0.30	0.22	0.26	-0.16	0.14	-0.23	-0.20	-0.14	-0.52

TABLE 3

Rank Correlation: York U. (May - Aug. 91)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	ISOPREN	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.95	0.74	0.91	0.86	0.89	0.90	0.89	0.89	0.81	0.63	0.72	0.89	0.90	0.90
C2H4	0.95	1.00	0.75	0.96	0.85	0.90	0.90	0.89	0.90	0.82	0.61	0.78	0.85	0.90	0.89
C2H6	0.74	0.75	1.00	0.80	0.88	0.82	0.81	0.83	0.84	0.87	0.29	0.79	0.82	0.85	0.81
C3H6	0.91	0.96	0.80	1.00	0.86	0.92	0.92	0.92	0.93	0.86	0.55	0.88	0.84	0.92	0.91
C3H8	0.86	0.85	0.88	0.86	1.00	0.93	0.93	0.94	0.95	0.96	0.33	0.79	0.95	0.91	0.87
n-C4H10	0.89	0.90	0.82	0.92	0.93	1.00	0.98	0.98	0.99	0.92	0.49	0.86	0.90	0.94	0.90
i-C4H10	0.90	0.90	0.82	0.92	0.93	0.98	1.00	0.99	0.99	0.93	0.52	0.86	0.91	0.95	0.93
n-C5H12	0.89	0.89	0.83	0.92	0.94	0.98	0.99	1.00	0.99	0.93	0.50	0.86	0.90	0.95	0.92
i-C5H12	0.89	0.90	0.84	0.93	0.95	0.99	0.99	0.99	1.00	0.93	0.49	0.87	0.91	0.95	0.91
n-C6H14	0.81	0.82	0.87	0.86	0.96	0.92	0.93	0.93	0.93	1.00	0.30	0.83	0.93	0.92	0.90
ISOPREN	0.63	0.61	0.29	0.55	0.33	0.49	0.52	0.50	0.49	0.30	1.00	0.40	0.43	0.55	0.58
BENZENE	0.72	0.78	0.79	0.88	0.79	0.86	0.86	0.86	0.87	0.83	0.40	1.00	0.71	0.79	0.74
TOLUENE	0.89	0.85	0.82	0.84	0.95	0.90	0.91	0.90	0.91	0.93	0.43	0.71	1.00	0.92	0.93
o-XYL	0.90	0.90	0.85	0.92	0.91	0.94	0.95	0.95	0.95	0.92	0.55	0.79	0.92	1.00	0.98
m,p-XYL	0.90	0.89	0.81	0.91	0.87	0.90	0.93	0.92	0.91	0.90	0.58	0.74	0.93	0.98	1.00

CN Tower Ground Level (Jul - Aug, 91)

	C2H2	C2H4	C2H6	C3H6	C3H8	n-C4H10	i-C4H10	n-C5H12	i-C5H12	n-C6H14	ISOPREN	BENZ	TOLU	o-XYL	m,p-XYL
C2H2	1.00	0.90	0.67	0.90	0.88	0.87	0.92	0.92	0.87	0.93	0.60	0.77	0.90	0.85	0.85
C2H4	0.90	1.00	0.63	0.95	0.89	0.87	0.90	0.90	0.87	0.93	0.59	0.67	0.75	0.72	0.72
C2H6	0.67	0.63	1.00	0.42	0.57	0.63	0.72	0.72	0.63	0.55	0.59	0.83	0.53	0.45	0.45
C3H6	0.90	0.95	0.42	1.00	0.92	0.83	0.85	0.85	0.83	0.93	0.54	0.58	0.80	0.78	0.78
C3H8	0.88	0.89	0.57	0.92	1.00	0.83	0.87	0.87	0.83	0.93	0.52	0.70	0.92	0.88	0.88
n-C4H10	0.87	0.87	0.63	0.83	0.83	1.00	0.98	0.98	1.00	0.82	0.54	0.82	0.83	0.85	0.85
i-C4H10	0.92	0.90	0.72	0.85	0.87	0.98	1.00	1.00	0.98	0.85	0.59	0.85	0.85	0.83	0.83
n-C5H12	0.92	0.90	0.72	0.85	0.87	0.98	1.00	1.00	0.98	0.85	0.59	0.85	0.85	0.83	0.83
i-C5H12	0.87	0.87	0.63	0.83	0.83	1.00	0.98	0.98	1.00	0.82	0.54	0.82	0.83	0.85	0.85
n-C6H14	0.93	0.93	0.55	0.93	0.93	0.82	0.85	0.85	0.82	1.00	0.71	0.60	0.73	0.70	0.70
ISOPREN	0.60	0.59	0.59	0.54	0.52	0.54	0.59	0.59	0.54	0.71	1.00	0.59	0.30	0.25	0.25
BENZENE	0.77	0.67	0.83	0.58	0.70	0.82	0.85	0.85	0.82	0.60	0.59	1.00	0.78	0.75	0.75
TOLUENE	0.90	0.75	0.53	0.80	0.92	0.83	0.85	0.85	0.83	0.73	0.30	0.78	1.00	0.98	0.98
o-XYL	0.85	0.72	0.45	0.78	0.88	0.85	0.83	0.83	0.85	0.70	0.25	0.75	0.98	1.00	1.00
m,p-XYL	0.85	0.72	0.45	0.78	0.88	0.85	0.83	0.83	0.85	0.70	0.25	0.75	0.98	1.00	1.00

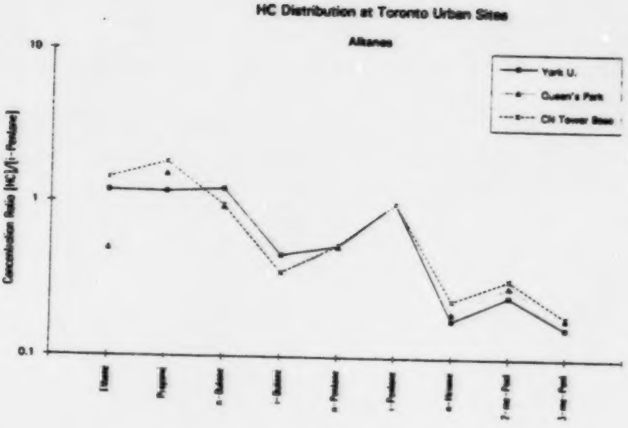

FIGURE 4

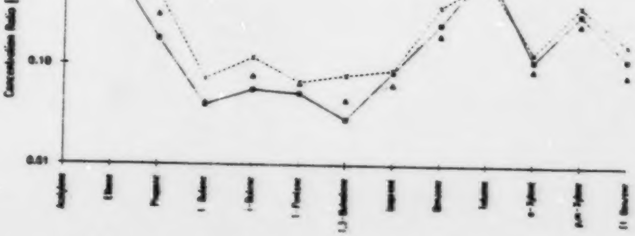

FIGURE 5

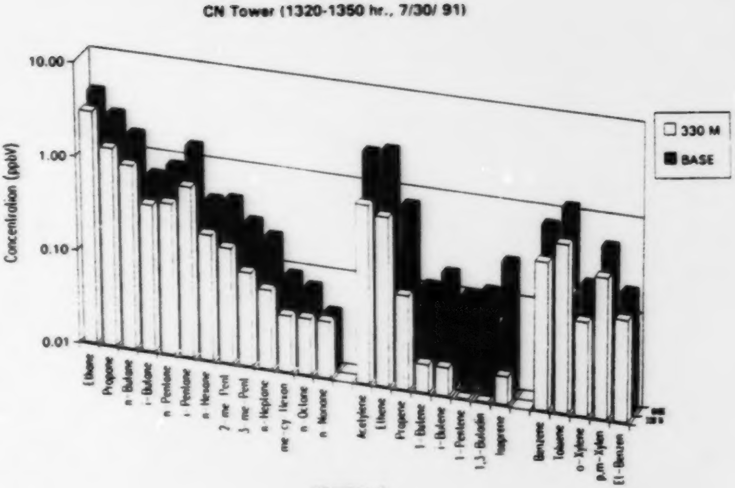
CN Tower (1320-1350 hr., 7/30/ 91)

FIGURE 6

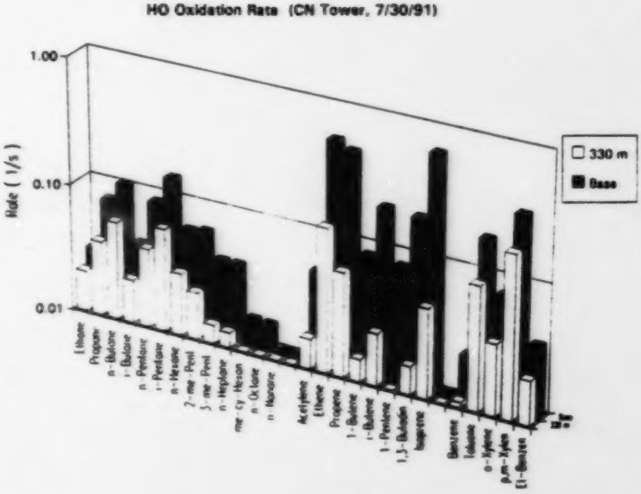
HO Oxidation Rate (CN Tower, 7/30/91)

FIGURE 7

A7

Analysis of Spatial and Temporal Distribution of Inhaleable Air Particulates in Ontario

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Abstract:

Source identification of airborne particulate matter is possible using a wide range of analytical techniques which can, in principle, supply the trace element and isotope distribution in specific particles. We have found that the kinetics of the conversion of sulphite ions to sulphate ions in solutions in contact with particulate matter is useful both as a means of source identification and as an indicator of the chemistry of a given air mass. The reactivity of the material can be combined with conventional analytical methods can be used in conjunction with spatial and temporal distribution data for source identification.

Introduction:

A wide range of sophisticated analytical techniques are available for the analysis of airborne particulate matter. In principle these yield information which should be useful in the identification of specific particulate sources. For instance, a given sample might be expected to contain a unique set of trace elements which could be further characterized according to their oxidation state and chemical environment (1) - (i.e. oxide or pure metal) and/or the isotope distribution of individual elements (2), which is often site-specific. Finally the reactivity of the particulate matter as a catalyst for specific atmospheric reactions is a potentially important indicator of their source. Accordingly we have obtained a bulk analysis of filter material using SIMS, ICP/MS, ICP/AES, XRF and SEM, in addition XPS, XRD, EM, and SAM have been combined with these techniques to establish the distribution and oxidation states of the various elements detected. These results have shown a ready distinction between material, principally clays, resulting from surface wind erosion and those from high temperature combustion dominated by iron oxides and fused alumino-silicate material. Mobile sources can be identified by the presence of significant amounts of amorphous carbon in conjunction with Br (3) from free radical scavengers in the fuel and, till recently, lead (4). Evidence suggests that the trace element distribution in the alumino-silicate material may be indicative of the origin of the sample while the nature and quantity of amorphous carbon is probably from inefficient combustion as in low temperature fires and poorly tuned diesel engines. Given ideal conditions credible source identification should be possible using complimentary results from this equipment, however, each instrument carries a unique set of problems. For instance SIMS is capable of detecting virtually all the elements and their isotopes but is a semi-quantitative technique, XPS while supplying the oxidation state of each element is sensitive only to surface atoms and is plagued by problems associated with charging of the sample. Application of the techniques is also time consuming and expensive. Chemical reactivity can be measured relatively rapidly and easily by using ion chromatography to monitor the rate of conversion of sulfite ion to sulfate ion in solutions in contact with air particulates. The results can be used to select particle assemblies showing unusual reactivity for further analysis, thus reducing the number of samples that receive intensive study and the kinetics observed may be used to indicate the most likely catalytic agents, which are in turn often site-specific

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Experimental:

The air sampling was carried out by the Ontario Ministry of the Environment using high volume sampling (Ca 1200 Litres per minute) for a twenty-four hour period at selected sites throughout Ontario using a high purity quartz filters. The collection equipment was so designed that the particles collected had an aerodynamic diameter of 10 microns and smaller.

The catalytic activity of the filters was measured by cutting a planchette having an area of 5 cm^2 from the centre of the loaded filter. This was then immersed in a solution 20 ppm in HSO_3^- at a pH maintained at 4.6 by an acetic acid/acetate buffer. The kinetics of the reaction:

$$2HSO_3^- + O_2 \rightarrow 2SO_4^= + 2H^+$$

were monitored at room temperature using a Dionex DX-100 Ion Chromatograph. $[SO_4^=]$ in solution prior to the addition of the HSO_3^- were used as an indicator of total loading on the filter. XRF data was used to estimate the concentration of various elements on the filter surface while ICP/AES and FAAS were used to monitor the concentrations of selected ions in solution with special attention to Fe, both because it is abundant on the filter material and Fe^{3+} is an important catalyst in the conversion of HSO_3^- to $SO_4^=$ (5).

Model systems were used to establish the kinetics to be expected from a series of standard materials which were suspected catalysts. Thus the catalytic activity of various clays, supplied by the Geology Department of the University of Western Ontario, metallic iron, iron oxide, goethite (FeO.OH) and Fe^{3+}, and that of pure graphite and graphite oxidized with H_2O_2 for 12 hours were studied.

Results and Discussion:

Figure 1 shows the reactivities of a large number of filters taken from different sites. The reactivity varies widely between individual samples. This confirms our hypothesis that the chemical reactivity, measured in this way can be used to identify filter material of special interest for further study. Figure 2 shows the variation in the reactivity of filters versus their total particulate loading as measured by the total sulfate present on the filter. No correlation is evident. This is an important result showing that the differences in reactivity observed between filters do not simply represent variable filter loading. Figure 3 shows the variation of reactivity with time at a single collection site. No clear pattern is evident. This is hardly surprising since weather conditions i.e. wind speed and direction, snow cover and precipitation will be important determinants of the amount and nature of the material collected. Those results show that it is possible to select a relatively small number of filters having high reactivity from very large set. The selection will not be biased toward heavily loaded filters nor will filters from specific sites be used unless weather conditions are favourable.

Carbon from various sources is often an important component in the particulate matter. Its catalytic effects vary widely as a function of surface area, physical form (i.e. graphite or amorphous carbon), and degree of oxidation.(6) In our work high purity graphite yielded a specific rate constant of 1.94 x 10^{-3} min^{-1} on oxidation with H_2O_2 this value increased to 1.59

x 10^{-2} min^{-1} for the catalytic conversion of sulfite to sulfate assumed to be first order in sulfite.(7) Carbon can be removed from filters by low temperature ashing. Filters showing high reactivity can be subjected to this procedure, if the resulting material no longer shows catalytic activity then carbon is responsible and further analysis of the surface area and functional group distribution on the carbon should be undertaken.

Metals are also important catalysts.(8) XRF shows the most abundant transition metal on the filters to be iron. Studies with model systems show that iron metal, Fe_2O_3 and FeO.OH are not catalysts while Fe^{3+} is. Figure 4 shows the reactivity as a function of the concentration of Fe^{3+} in solution in a model system while Figure 5 shows the reactivity of the system as a function of Fe^{3+} in contact with the filters. This latter figure shows a good correlation between $[Fe^{3+}]$ and reactivity, but approximately 25% of the data points are anomalous. The anomalous data points indicate that either an inhibitor or second catalyst may be present in the filter material. Figure 6 shows the individual filter reactivity versus iron coverage as determined by XRF. Failure to achieve a good correlation is evidence for the presence of iron in relatively insoluble form which implies Fe in clay and/or Fe_2O_3 from smelting operations.

Finally clay minerals have been identified as catalysts and thus high reactivity may often result from clay minerals. The rare earth content of the clays may well be site specific. In addition our results show that the activity of illite clays is inhibited by phosphate ion. The mechanism of inhibition and the probable relationship to phosphate fertilizer and to agricultural activity is currently under investigation.

Conclusions:

The wide range of analytical equipment currently available should, in principle, allow source identification of specific air particulates using element and isotope distribution in conjunction with the chemical form and reactivity of the sample. The wide range of measurements required are however difficult, time consuming and expensive, as well failures are always possible because of the inherently small sample size.

Catalysis by material trapped on high volume filters can be studied relatively easily using IC to measure the kinetics of the conversion of sulfite to sulfate. So far we have identified three major catalytic systems: amorphous carbon, alumino-silicate minerals (clays) and metal ions (principally Fe^{3+}). Filters showing high reactivity may be selected for further, detailed analysis. In any event, considerable information indicative of the source can be obtained from the sulfite/sulfate reaction kinetics, for instance oxidized amorphous carbon appears to be more reactive than pure material. The former results from low temperature oxidation. Our studies on carbon reactivity are at an early stage and the literature indicates that our own limited results are not conclusive and that this area is poorly understood. The usefulness of the carbon for source identification remains problematic. Clay minerals, when present in their unaltered form contain site specific trace elements. Altered clay minerals (spherical glasses) are evidence of high temperature combustion. The suite of unreactive iron is indicative of iron in clays or iron oxides while Fe^{3+} is probably from metallic iron and is indicative of smelting or ore processing operations.

Kinetic measurements of the kind described here yield significant information about the nature of the particulate matter on individual filters. These results combined with detailed surface and chemical analysis are good indicators of the origin of specific sample material.

Glossary:

EM	Electron Microprobe
FAAS	Flame Atomic Absorption Spectroscopy
IC	Ion Chromatography
ICP/MS	Inductively Coupled Plasma/Mass Spectrometry
ICP/AES	Inductively Coupled Plasma/Atomic Emersion Spectroscopy
SAM	Scanning Auger Spectroscopy
SEM	Scanning Electron Microscopy
SEM/EDX	Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis
SIMS	Secondary Ion Mass Spectrometry
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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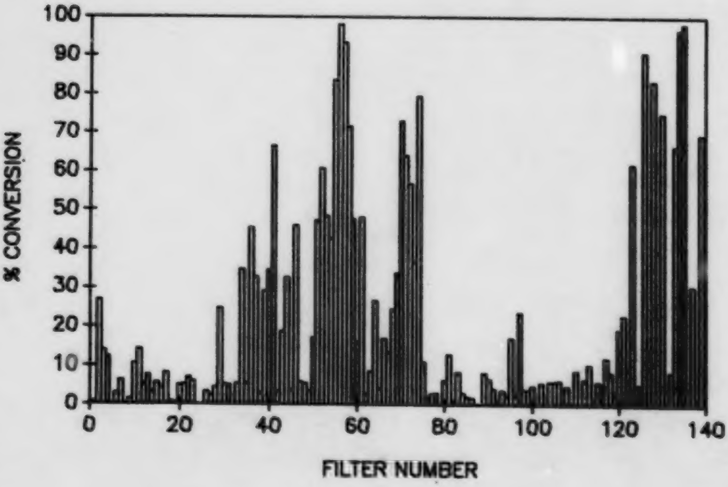

Figure 1. % Conversion for the catalytic oxidation of S(IV) to S(VI) showing the variation in reactivity for filters from different sites.

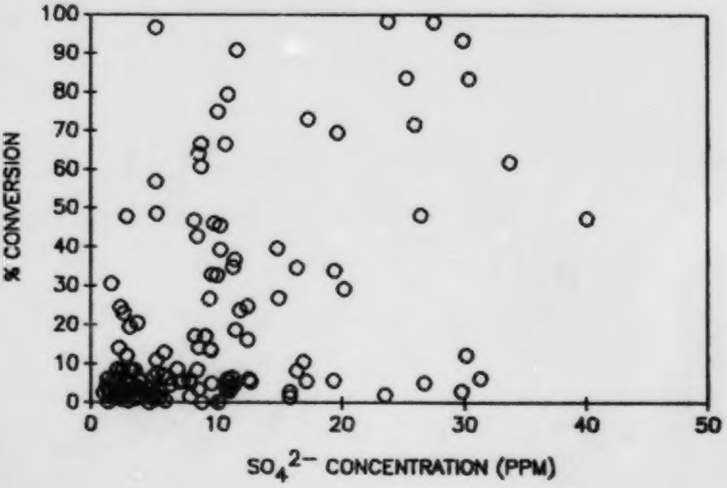

Figure 2. % Conversion versus SO_4^{2-} concentration on filters.

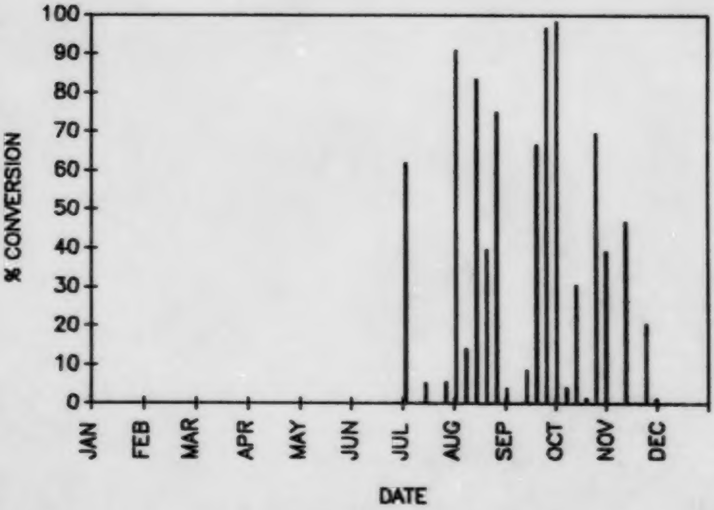

Figure 3. % Conversion for station 71342 as a temporal distribution.

(Note: PM_{10} sample collection started July 3, 1989.)

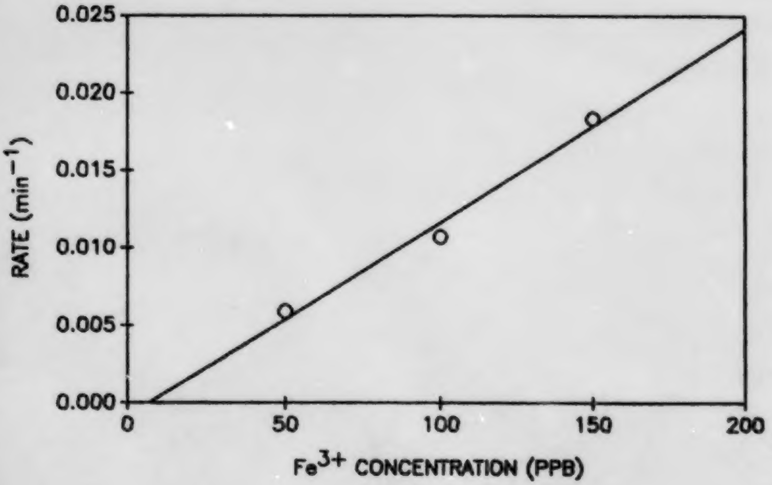

Figure 4. Rate constant versus Fe^{3+} concentration in model system for the catalytic oxidation of S(IV) to S(VI) at pH 4.7.

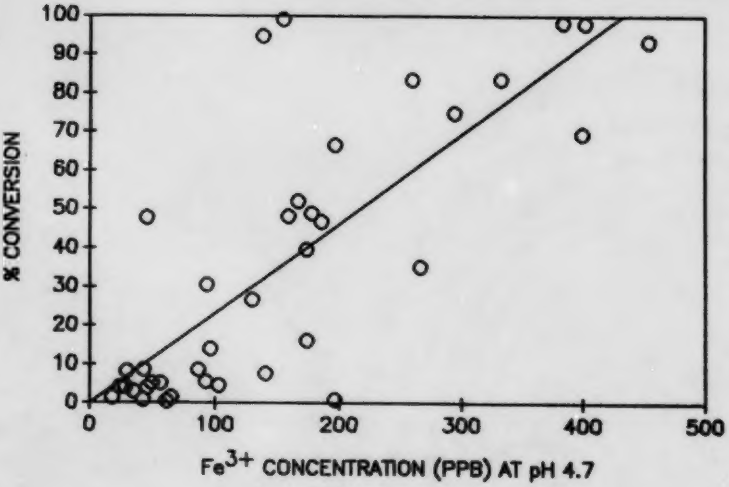

Figure 5. % Conversion versus Fe^{3+} concentration of filters at pH 4.7 for the catalytic oxidation of S(IV) to S(VI).

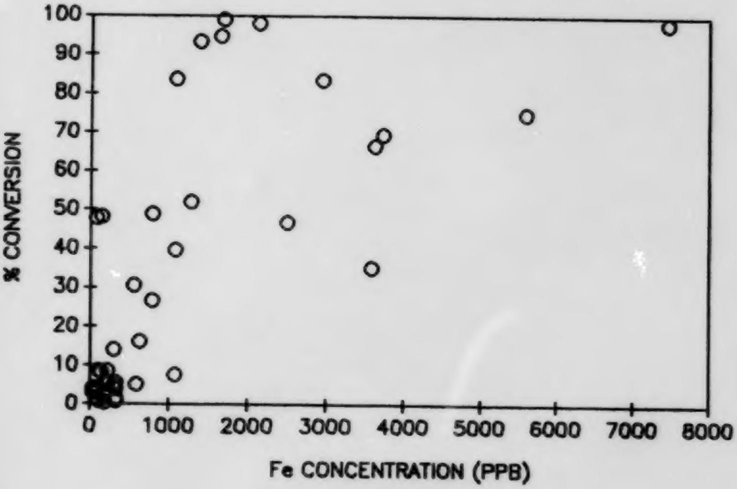

Figure 6. % Conversion versus Fe concentration as measured by XRF (Ontario Ministry of the Environment).

(Note: µg/m^3 converted to our units (ppb) by conversion factor 1 µg/m^3 equal to 37.27 ppb.)

A8

THE APPLICATION OF DIRECT TRILINEAR DECOMPOSITION (DTD) TO REAL AIRBORNE PARTICLE COMPOSITION DATA

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Abstract

Air quality data are typically obtained from samples taken at a number of sites at various times and which are then analyzed for a number of species. Thus, a 3-way data set is obtained that represents the spatial and temporal variations in the composition of the atmosphere. Specifically airborne particle samples are taken and analyzed for multiple elements to provide a suite of elemental concentrations over the space and time frames of the sampling network. Previously we presented the results of a methodological study of a new method for analyzing such 3-way data call the Direct Trilinear Decomposition (DTD). Using simulated data, DTD proved to be a quantitative model with potentially high power to identify particle sources as well as transformations in composition during transport. We have now applied this approach to regional scale data from the SCENES network covering the southwestern United States. The results of these studies are presented here.

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INTRODUCTION

In last two decades, receptor modeling has played a larger and larger role in air quality management.[1234] In receptor modeling, ambient samples are collected and characterized for variety of chemical species. The ambient concentration data are then analyzed using the model. From the output of the model, the sources of pollutants are identified by their chemical composition (called "source profile") and the mass contributions of the sources to the samples are estimated. The most commonly used models are chemical mass balance (CMB), factor analysis, and target transformation factor analysis (TTFA).[3,4]

Generally, receptor modeling methods are one-mode or two-mode models. These models work with a data vector or a two-dimensional data matrix. For example, a vector containing concentrations of chemical species for a single ambient sample, or a matrix constructed of the ambient concentrations of a number of chemical constituents measured during a series of sampling periods at a single location. There are many air quality monitoring networks that routinely collect samples from multiple sites and analyze the samples for variety of species. Therefore, the data gathered are three-way blocks with one way for species, one for sites, and one for sampling periods (Figure 1). The one-mode and two-mode models use only a part of the data block, i.e., a column or a slice in the block. With these models, one can not analyze the whole data block at once, and thus can not simultaneously examine the spatial and temporal variations.

We previously presented the results of a methodological study of a method called direct trilinear decomposition (DTD).[5] The goal of this approach is to provide a three-mode receptor model that produces source profiles and mass contributions. The development of the DTD model has evolved from the work by Sanchez and Kowalski[6]. They developed DTD to process

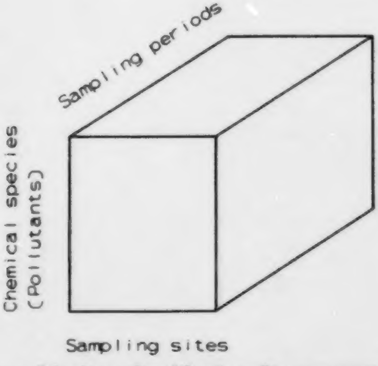

Figure 1. Typical structure of the data gathered for air quality management.

data obtained in analytical chemistry with instruments that generate two-way arrays of data for multiple samples. Their example was a three-way data set of emission-excitation fluorescence spectra for three mixtures of three organic compounds. With their DTD method, the emission and excitation spectra of all three compounds were predicted and the relative concentration of the compounds in the mixtures were calculated. Burdick *et al.* independently developed a similar method and successfully applied to an excitation-emission-frequency array[7].

In order to adopt DTD in receptor modeling, a major difficulty had to be overcome. This problem was how to relate pollution sources to the model. In the example of Sanchez and Kowalski, each organic compound had two spectra, an emission spectrum and an excitation spectrum.[6] In fact, DTD model is applicable for a multiple sample system with two-dimensional spectral surfaces. A source profile in a receptor modeling problem can be considered to be one spectrum. Then another spectrum-like property of the pollution source is needed. This problem and others concerning the application of DTD in receptor modeling were resolved by methodological studies using simulated data sets. The preliminary application of this new technique was conducted to analyze simulated data sets and it showed good performance. Thus, it has been applied to a data set taken from SCENES data base[8].

THEORY

The Trilinear Model

The following equation represents the trilinear model.[6]

$$X_{ijk} = \sum_{n=1}^{N} a_n \otimes b_n \otimes c_n + E_{ijk} \tag{1}$$

Note that X_{ijk} and E_{ijk} represent three-way matrices, and x_{ijk} and ϵ_{ijk} are their corresponding elements. X_{ijk} is observed data matrix and E_{ijk} is model error term. Vectors a_n, b_n, and c_n are n-th column vectors of matrices A, B, and C, and they represent spectrum or profile of n-th component in the first, second, and third mode, respectively. The vector a_n is an I dimensional vector, b_n is J, and C_n is K. Equation (1) can be rewritten in scaler form:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} + \epsilon_{ijk} \tag{2}$$

A detailed description, discussion, and the algorithms for performing a trilinear decomposition based on the model in equation (1) can be found in Sanchez and Kowalski.[6]

The key to applying DTD in receptor modeling is to establish the relationship between the terms in the model [equation (1)] and the physical properties of the airshed. If the three-way data matrix is arranged such that mode 1 (*i*) corresponds to the chemical species, mode 2 (*j*) to sampling period, and mode 3 (k) to site, the N vectors $\{a_n\}$ can represent the source profiles. The following two new concepts are introduced so that the model can be fitted into the physical system.

Emission patterns refer to the relative variations of source emission strength changing with time at the receptors. Like a source profile, the emission pattern can be considered to be another property of a source. Each source has its own emission pattern. With the source profile and emission pattern, a source can be characterized more completely and accurately. The vectors $\{b_n\}$ in model (1) correspond to the emission patterns. As eigenvectors, $\{b_n\}$ are independent to each other. Real emission patterns are not necessarily independent. The term "emission pattern" used in this work is a concept with which the characteristic of real emission pattern of a source can be described. It is similar to representation of a source profile by a principle factor in factor analysis. The emission pattern will show the most important feature of a real world emission pattern.

Another concept, "site coefficient", is introduced to refer to the vectors $\{c_n\}$ in equation (1). The site coefficients indicate the variation in source strength from site to site. With these definitions, a three-way air quality data set could be decomposed into source profiles (a_n), emission patterns (b_n), and site coefficients (c_n). However, each of these profiles is a relative profile, and its values may not agree with actual physical scales.

The ultimate goal of receptor modeling is not only to identify sources, but also to apportion the sample mass among the sources. In order to estimate the mass contributions, a matrix reconstruction procedure is introduced after DTD. The mass contribution of source n at site k in period j, $\bar{z}_{njk}$, can be obtained by combining the emission pattern and the site coefficient.

$$\bar{z}_{njk} = b_{jn} c_{kn} \tag{3}$$

If the source profile $\bar{y}_{in}$ is defined as

$$\bar{y}_{in} = a_{in} \tag{4}$$

the model in scaler form becomes:

$$x_{ijk} = \sum_{n=1}^{N} a_{in} b_{jn} c_{kn} = \sum_{n=1}^{N} \bar{y}_{in} \bar{z}_{njk} \tag{5}$$

The scale of $\bar{y}_{in}$ and $\bar{z}_{njk}$ do not necessarily agree with the actual scale of source profiles and mass contributions. Similar to TTFA, a regression procedure can be used to find a set of scaling coefficients, $s = \{s_n\}$, such that

$$x_{ijk} = \sum_{n=1}^{N} \left(\frac{\bar{y}_{in}}{s_n} \right) (s_n \bar{z}_{njk}) = \sum_{n=1}^{N} y_{in} z_{njk} \tag{6}$$

where y_{in} and z_{njk} are the scaled source profiles and contributions. The regression is based on

$$mass_{jk} = \sum_{n=1}^{N} z_{njk} = \sum_{n=1}^{N} s_n \bar{z}_{njk} \tag{7}$$

Determination of number of factors (number of sources in receptor model), N, is always an important issue in any factor models. In two-mode methods, there are several function or indicators that are used to investigate the number of factors.[3,4] In three-mode models, however, the methods of determining number of factors are very limited. Number of factors are basically chosen by eigenvalues. Sanchez and Kowalski suggested "that a slight overdetermination of N does not affect the resolved spectra as much as underestimation", but they did not give a better way to resolve this question.[6]

APPLICATION

An example of DTD application is given in this section. DTD has been applied to a real data set from SCENES data base.[7] SCENES is a sampling and analysis program that has yielded a large atmospheric environmental data base. Its sampling network includes portions of California, Nevada, Arizona, and Utah (Figure 2). The data residing in the data base include the chemical compositions of two size fractions of particles, visibility measurements, meteorological measurements, and gaseous air pollutant measurements. The chemical composition data of particles are suitable to DTD application. Since the total particulate samples (<15 μm, aerodynamic diameter, AD) have more chance to be influenced by a number of local sources and the fine particulate samples (<2.5 μm AD) should have sources distributed over the whole region, the fine particulate data were used in this study.

The samples were collected on Teflon and quartz filters and analyzed using established methods: X-ray fluorescence (XRF) for trace elements, thermal extraction for carbonaceous materials (organic and elemental carbon), and ion chromatography for ions (sulfate, nitrate, and ammonium). The ionic species data were not available at the most of the sites. The concentration of some elements were always near the filter blank values. These data were not used in this study. Fifteen species were included in the analysis. They were Al, Si, P, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Br, Pb, ROC (residual organic carbon), and EC (elemental carbon).

There are eleven observation sites (Table 1). Aerosol samples are collected at seven of them. The site MC (see Figure 2) has very limited data so that six sites (BY, GC, HI, HP, MV, and SM) were included. The data used were for 24 hours samples collected every day. These data were available from March 1986 to February 1987. In order to get a complete three-way data set, the sampling periods (dates) were selected such that all six sites have valid data within common periods. By this criterion, forty six periods were selected. The DTD computer code was developed using MATLAB software package. Since the MATLAB version used in this work was

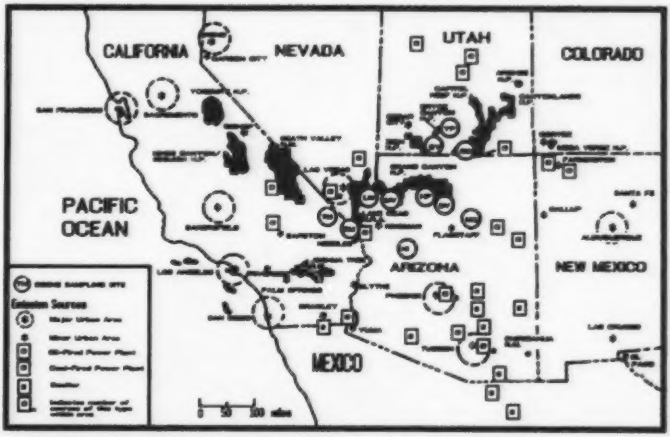
CALIFORNIA
NEVADA
UTAH
COLORADO
PACIFIC OCEAN
ARIZONA
NEW MEXICO
MEXICO
Emission Sources
0 50 100 miles

Figure 2. Air quality and visibility observation sites in the SCENES area.

Table 1. SCENES observatories and types of aerosol samples collected

Site designation	Map description	Aerosol[a]
HI	Hillside, AZ	TP, FP
MC	Meteor Crater, AZ	TP, FP
TM	Turquoise Mountain, CA	--
SM	Spirit Mountain, NV	TP, FP; PM-10 (HV)
MV	Mead View, NV	TP, FP; PM-10 (HV)
LM	Lake Mead, NV	--
HP	Hopi point, AZ	TP, FP; CP, FP (SFU)
DV	Desert View, AZ	--
GC	Glen Canyon, AZ	TP, FP; CP, FP
BY	Bryce Canyon, UT	TP, FP; CP, FP (SFU)
YP	Yovimpa Point, UT	--

[a] abbreviations:
TP=total (<15 μm AD) particulate matter;
FP=fine (<2.5 μm AD) particulate matter;
CF=coarse (>2.5 μm AD) particulate matter;
SFU=stacked filter units

PCMATLAB that limits the number of entries in a matrix variable to 8188. In this case, the number of periods can not be more than 15. The periods between April and June were used, and there were 12 valid periods. Therefore, the data matrix was 15 (species) x 6 (sites) x 12 (periods).

The data matrix was analyzed using DTD. Only two sources were retained in the solution. In this particular case, three or more retained sources will cause complex solutions. Tables 2 and 3 and Figures 3 and 4 present the results. Since species covered representative components in both inorganic and organic matters, total sample masses were used to scale the results [see equation (7)]. If only inorganic matter was measured, one may find an average percentage of inorganic matter in the sample mass, and use that percentage of mass to scale the results.

According to the chemical compositions (source profiles in Table 2), sources 1 is identified as soil. The major elements of soil are Si, Al, S, Ca, Fe, K, and organic carbon. Source 2 consists of S and organic compounds with small amount of K and element carbon. This source appears to be secondary sulfate because of high S content. However, the concentration of organic compounds and K suggest that it may include emissions from vegetation or wood smoke. This source would be broken down further if there were no complex solution problem. The complex solution problem has been encountered in the simulation study when great fluctuation of source composition occurs (equivalently when the fundamental assumption on constant source profiles in receptor model is significantly violated) or when smaller fluctuations and very high collinearity are combined. This problem could be minimized by properly designing sampling program.

Figure 3 shows an increasing trend in emission strength of both sources from April to

Table 2 Source profiles predicted by DTD based on the SCENES data set (Unit: %).

No.	Species	Source 1	Source 2
1	Al	6.36	0.55
2	Si	19.18	-1.03
3	P	0.16	0.31
4	S	5.39	12.76
5	K	1.61	2.40
6	Ca	3.97	-1.41
7	Ti	0.24	0.01
8	Mn	0.05	0.01
9	Fe	2.12	0.16
10	Cu	0.01	0.02
11	Zn	0.03	0.06
12	Br	0.04	0.14
13	Pb	0.05	0.09
14	ROC	9.00	21.88
15	EC	0.89	3.07

Table 3. The site coefficients for the SCENES data set

Site	Source 1	Source 2
BY	1.97	0.96
GC	2.87	1.27
HI	1.23	3.28
HP	2.57	1.52
MV	2.32	1.80
SM	2.72	1.97

May. This emission pattern information may be helpful in identifying sources when two sources have similar profiles. The emission patterns should be interpreted better when considering meteorological conditions and significant pollution episodes.

The effects of the sources on the sites can be seen in Table 3 of the site coefficients. Within the studied periods, soil (source 1) has larger influence on all the sites except site HI. At site HI, sulfate (source 2) is a much more important source than soil. The study by Malm *et al.*[9] suggested that southern Arizona was a sulfur source area influencing the Grand Canyon. There are numerous copper smelters in southern Arizona that emit significant amount of SO_2. HI is the

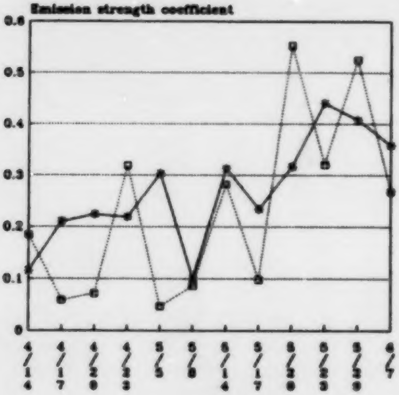

Figure 3. The emission patterns of two sources identified from the SCENES data set.

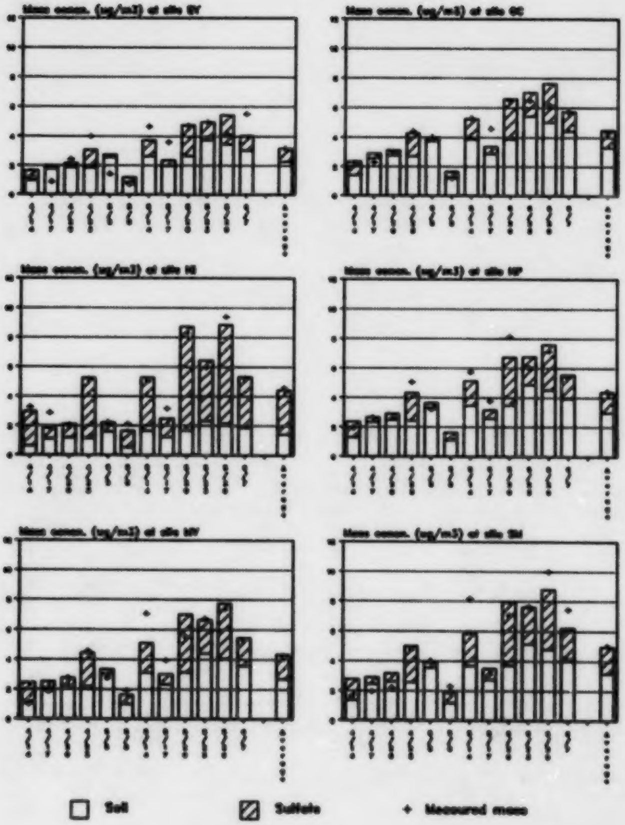

Figure 4. The source contributions predicted by DTD based on the SCENES data set.

closest site to these sources.

The mass contributions of identified sources to every samples are estimated and plotted in Figure 4. Since the results are regressed to measured total sample mass [equation (7)], the calculated total sample mass is overestimated for some samples, and underestimated for the others. In average, however, the predicted mass matches the measured mass. The impacts of sources to each site in every period can be seen in this result.

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A10

STABILIZATION OF WASTE IN A LANDFILL ENVIRONMENT.

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INTRODUCTION

The use of landfill disposal continues to be the most widely used system for disposal of municipal refuse and industrial wastes. Despite the long history of landfill use, the impact of the landfill on the surrounding environment and aquifer remains controversial. Although the initial gross content of the landfill can be estimated with reasonable accuracy, the rate and extent of material transfer to the environment is not well defined. Part of the difficulty is in identifying and quantifying the parameters that control the chemical and biological reactions occurring within the landfill mass. Knowledge of these parameters is critical in determining environmental impact and in improving the design of landfill sites. Some of the questions that need to be addressed from the perspective of landfill liner design are: what becomes of wastes in the landfill?; how long will leachate generated from the landfill pose an environmental threat? There are also questions of a fundamental nature. What types of waste decompose, convert, react, stabilize or migrate? Indeed, what is our current level of understanding of waste stabilization?

One approach to developing an understanding of the landfill environment is to measure and monitor the effluents which leave the system. This is an approach is best performed in contained cells so that a mass balance can be conducted. The cells should be sufficiently large to behave in the same manner as a landfill in the environment. The results of our work using this approach have been reported in previous conferences.

A second method of investigating the landfill environment is to dig up an existing site and analyze the remaining contents. A fascinating report was recently given in the National Geographic[1] using this approach. From this work one is led into the realm of archaeology and the disposal habits of current and previous generations. The identification of well preserved food stuff, clothing, paper and plastic goods in this work has demonstrated the uniqueness of the environment where anaerobic conditions can prevent the decay of materials that would have decomposed on the surface. Upon seeing newspaper that is still legible after 10 or 15 years in the ground one might be tempted to think that this is an unchanging environment but the external leachate monitoring tells a different story.

From the leachate analysis the chemistry of the landfill environment is revealed. Over a period of several years the amount of acid generated from organic decomposition decreases, the concentration of metals in the leachate decreases and the leachate loses its colour and odour and the anaerobic conditions begin to decline. From the external perspective the landfill appears to be approaching an inert state or stabilized state. Yet, what is seen within the landfill are the relatively undecomposed original major constituents. Why are the two perspectives at odds? In the first place, there is no well defined association between the components put into the landfill and the resulting leachate composition. The current perception is that if a waste can release contaminants in water (or acetic acid) then those contaminants will appear in the leachate if that waste is deposited in the landfill. However from studies of contaminant migration in soil and ground water, researchers have often recognised the loss of contaminants and assumed that dispersion, precipitation or bio-mitigation effects have prevented the tracking of some of the contaminants. Indeed, often there is difficulty in finding a tracer that will not be lost to the ground matrix. Movement of contaminants in a landfill environment encounter an even greater variety of non-ideal conditions. The chemical environment can change spatially and temporally.

These changes may be gradual or have relatively sharp transitions. These environments also define the microbial population and perhaps mobilization forces. The values of pH, Eh and co-contaminant species such as sulphides and organic by-products may play an important role in the mobility of contaminants. Only in the case of wastes containing very soluble ions such as chloride and sodium does the leachate show (or usually show) the presence of the added contaminants.

In this work, the process of stabilization within a landfill environment is described. The interactions of MSW leachate and a surrogate waste have been investigated from a microscopic perspective since the macroscopic view does not explain satisfactorily the landfill behaviour.

EXPERIMENTAL

This study has employed large scale laboratory leaching columns which were designed to simulate landfill behaviour. There are 16 columns in operation packed with 4 different compositions: 100% municipal solid waste(MSW), MSW + 8% industrial waste(IW), MSW + 30% IW and 8% IW in sand. The high density polyethylene cylindrical columns are 1.93m high, and 0.33m in diameter and contain approximately 43 kg (dry weight) of MSW. One half of the columns receive moisture input from precipitation while the other half receive controlled periodic water additions. The systems were maintained in unsaturated flow conditions with regular leachate removal from the bottom reservoirs. As a result of their size the columns are operated in an outside location. This scale of experimentation, though large for laboratory studies, is required for developing the landfill hydrodynamics and biological activity.The role of hazardous waste was studied using a selected hazardous waste at 8 and 30 weight percent of the municipal refuse content. The waste was added in 3 layers in the test cells.

At the end of a 5 year period selected columns were taken to a cold room and were frozen at a temperature of -15°C. The columns were then sectioned vertically and sampled by taking cores for chemical analysis or cutting sections for electron and optical microscopic analysis. All samples were dried under vacuum and weighed before analysis. Samples that were cut for microscopic analysis had to be dried under slight compression to maintain sample integrity. These dried samples were encapsulated in resin, then were cut and polished for examination.

Chemical analysis was performed using ICP and INAA. Electron microscopy was performed with a Hitachi SEM with EDX for both X-ray microanalysis and elemental X-ray mapping.

RESULTS AND DISCUSSION

The leachate from the four MSW columns satisfactorily simulated landfill behaviour. The concentrations of 8 elements in the leachates from these columns are shown in Figure 1. Concentrations of all contaminants have declined with time.

The concentration of 8 elements in the leachates from the four MSW columns containing a total of 8% industrial waste is shown in Figure 2. Again the concentrations of all contaminants in the leachate have declined with time.

The comparison of COD and pH for these 8 columns is shown in Figure 3. The most notable difference in the leachates is that the presence of the industrial waste has resulted in lower concentrations of most of the metals and COD. In addition, the pH of leachate from the columns with industrial waste was more rapidly neutralized, although this characteristic also was noted in one of the MSW columns.

The analysis of the industrial waste (Table 1) shows that there was the potential for a significant input of several metals to the leachate. However, using the Ontario Ministry of the Environment LEP, the industrial waste only had significant calcium and lead as leachable components but the lead values were sufficient to have the waste classified as hazardous (Table 1). More important however, was the alkaline content of the waste, which was sufficient to maintain the liquid at pH= 12 during the LEP test. Thus there was considerable uncertainty whether the LEP test which determines chemical leachability would predict the behaviour in a landfill.

The very obvious difference in the leachates from the two sets of columns is that the presence of the industrial waste appeared to inhibit the level of contaminants (Table 2). There have been several theories proposed to account for the low level of leachate contamination from the columns having industrial waste present. The first is that the waste may form a compact or slimy layer which blocks the flow of water through the column and results in channelling and hence low metal extraction. The second is that any metals solubilized from the industrial waste would encounter sulphur species in the MSW and because of the reducing conditions would precipitate as insoluble metal sulphides. These might encapsulate the waste particles and mitigate leachate contamination. The third theory is that the alkalinity of the industrial waste layer would serve to precipitate dissolved metals passing through the layer and thus only the MSW below the bottom industrial waste layer would contribute to the leachate contamination. The fourth theory is that the alkalinity released by the industrial waste layers inhibit microbial action and hence lessen leachate contamination. The fifth theory is that metal ions released by the industrial waste inhibit microbial action and hence lessen leachate contamination. The validity of these theories are being investigated in this study by analyzing the waste after the 5 year test period.

The pH values of various layers in the columns were measured by taking cored samples, from the frozen sectioned column, slurrying them in deionized water and measuring the pH. Figure 4 shows the measured pH values as a function of position in the column and the position of the industrial waste layers. At the start, the industrial waste layers were very alkaline with a pH value of >12. From the measurements shown at the end of the 5 year period, the topmost layer has almost been neutralized, while the middle and bottom layers have retained a little alkalinity. Apart from the IW layers, the pH of the MSW is essentially neutral regardless of the proximity to the IW layers. pH values from the MSW columns without industrial waste show a slight acidity.

Microscopic examination of the industrial waste layers and the surrounding MSW shows that a very sharp demarkation between the industrial waste and the MSW has been maintained. There is no evidence of solids from the industrial waste having been carried into the MSW. Careful examination of the top IW layer has shown the presence of fine channel structures in the upper portion and porosity in the lower region. The middle layer and lower layers show progressively less of the channel structure. Porosity is evident in all the layers. There is no evidence that the IW has formed a leachate barrier or that leachate did not pass through the layers. Indeed for the top layer of the industrial waste to have been neutralized and the middle and bottom layer to have been partially neutralized, means that acidified leachate must have passed through the layers. Preliminary X-ray microanalysis of the residue of the bottom layer (Table 1) shows that there has been a 5% loss of calcium from the IW matrix. This is consistent with the change of pH over time.

Analysis of Fe in the bottom waste layer (Table 1) has not shown any significant iron loss and this is consistent with the optical microscopy work which shows little corrosion of the iron oxides. There is microscopic evidence of an alkaline attack of iron silicate particles, however the leachate from the columns with IW had lower iron content than the MSW columns. Both types of columns showed corrosion of ferrous articles in the MSW layers.

From the X-ray analysis there is evidence that some zinc may have leached from the IW layer though there was no increase in zinc in the leachate. More detailed analyses are being conducted to determine the minor element stability. A chemical analysis of this layer using a nitric acid extraction has shown that there remains approximately 8% soluble Ca, 4% Fe, 6% Zn, 1.3% Pb and 0.02% Cd. These elements appear to retained in the IW because of their low solubility under alkaline conditions. Thus, except for calcium and zinc there appears to be little change to the bulk of the IW during the stabilization.

Analysis of the interface between the MSW and the IW by X-ray microanalysis and elemental mapping revealed clear evidence of calcium enrichment at both the upper and lower interfaces of each IW layer. The preliminary analysis of the two interface regions for the bottom waste layer is shown in Table 1. The Ca enrichment appears to be the result of precipitation in the form of calcium carbonate. Only at the lower interface of the bottom IW layer was a minor amount of sulphur detected. Although some calcium deposition was noted in the MSW near the interface, most appeared to be deposited in the IW layer. This suggests that the movement of CO_2 or carbonic acid into the layer was responsible for calcium carbonate formation. The enrichment at the top of the layer is from the movement of calcium rich leachate (as bicarbonate) down the column to the alkaline layer where calcium carbonate is formed. Within the IW layer calcium hydroxide migrates to the lower boundary where it deposits as calcium carbonate due to the presence of carbonic acid. There was no evidence of precipitation of any other metal at the interface regions. Thus the theory that the pH boundaries between MSW and an alkaline layer can serve as a filter for migrating ions was not observed except for calcium which was relatively concentrated. Similarly there was little evidence that sulphide precipitation served as a significant metal removal mechanism. Sulphides are generally highly visible in optical microscopy and there was no evidence for their presence. The minor sulphur content at one of the lower interfaces could have been from sulphate rather than sulphide compounds.

CONCLUSIONS

The following conclusions are based on the initial analysis of the waste stabilization process.

1. The industrial waste tested has not contributed to the contamination of the leachate from MSW in the experimental landfill columns. The LEP test had indicated that lead solubilization would be excessive.
2. The presence of the industrial waste in MSW has had the effect of decreasing the COD and metal ion contamination of the leachate.
3. The beneficial effect of the IW in MSW is not due to the formation of impermeable barriers or to the precipitation or adsorption of environmentally important metal ions in the leachate. Only calcium has been seen to enrich at both the upper and lower MSW/IW interface regions. The precipitation at the upper boundary is from reaction of downward flowing calcium bicarbonate with the calcium hydroxide in the IW layer. The enrichment of calcium carbonate at the lower interface is from the migration of calcium hydroxide in the IW which is neutralized by carbonic acid at the MSW interface. No other metals were found to be enriched at the interfaces.

4. The neutralization of an alkaline waste does not occur rapidly even when there is MSW leachate flow through the material. Two of the three IW layers have pH levels >8 after 5 years in the landfill cells.

5. Within the IW layer there is little evidence of dissolution of the residual particles with the exception of the alkaline attack of some iron silicate phases. There has been some solubilization of zinc from the industrial waste though there is no evidence of precipitation at the MSW interface or enrichment of the leachate.

6. The mineralogical investigation techniques with X-ray microanalysis and elemental mapping have proved to be very important tools in the investigation of waste stabilization.

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TABLE 1

ANALYSIS OF THE INDUSTRIAL SOLID WASTE

ELEMENT	Fe	Zn	Ca	Mn	Pb	Cr	Cd
Initial Mass in 43kg	851g	441g	388g	128g	61.7g	6.57g	1.02g
Initial Weight %	26.8	14.1	11.9	4.01	1.99	0.21	0.04
"Stabilized" Bottom Layer Analysis							
Bottom IW Layer (wt%)	27	11	7	4	-	0.3	-
Bottom IW Layer Upper interface (wt%)	21	11	15	3	-	0.3	-
Bottom IW Layer Lower interface (wt%)	25	6	13	2	-	0.3	-
Percent Extraction by OMOE LEP*	0	0.08	65	0.002	18	0.02	-
Percent Extraction by acid at pH= 5.5	6.4	52.3	88.5	8	50	17	70

*pH of LEP test was still 12.2 after maximum acid addition.

TABLE 2

TOTAL MASS OF ELEMENT LEACHED DURING STABILIZATION

Element	Fe	Zn	Ca	Mn	Pb	Cr	Cd
MSW (g)	176	5.3	291	4.4	0.11	0.01	0.02
MSW +8%IW (g)	25	0.3	106	1.2	0.03	0.02	0.02

Values from column #3 (MSW only) and column #7 (MSW + 8% IW). The total volume of leachate was approximately 350 L for each column.

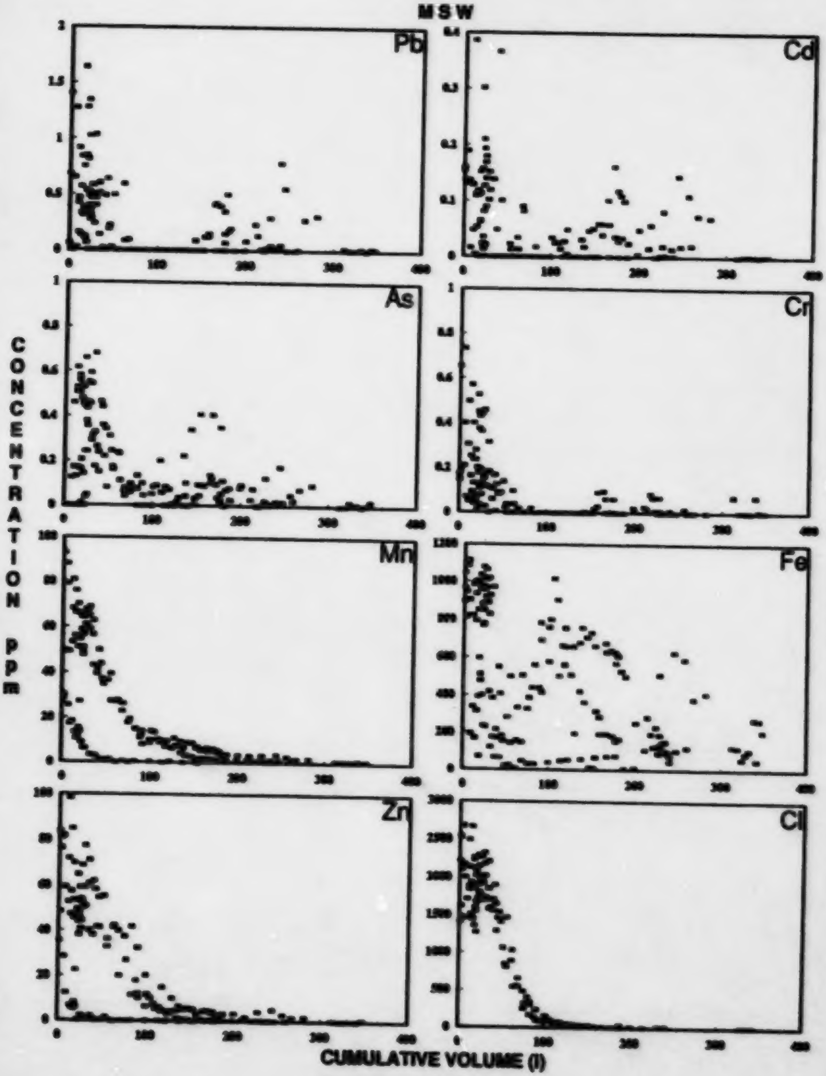

M S W
Pb
Cd
As
Cr
Mn
Fe
Zn
Cl
CONCENTRATION ppm
CUMULATIVE VOLUME (l)
0
0.5
1
1.5
2
0.1
0.2
0.3
0.4
0.2
0.4
0.6
0.8
20
40
60
80
100
200
400
600
800
1000
1200
500
1000
1500
2000
2500
3000
100
200
300
400

Figure 1

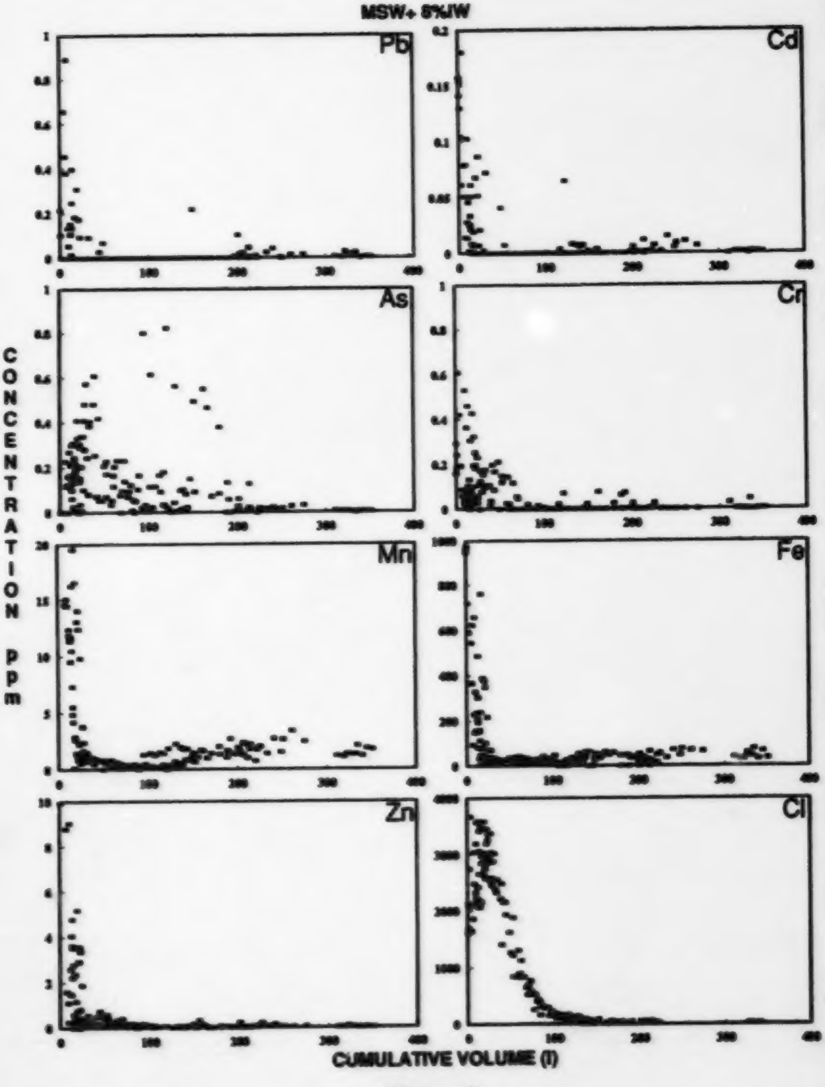

MSW+ 5%JW
Pb
Cd
As
Cr
Mn
Fe
Zn
Cl
CONCENTRATION ppm
0
0.2
0.4
0.6
0.8
1
0.05
0.1
0.15
5
10
15
20
200
400
600
800
1000
2
4
6
8
10
1000
2000
3000
4000
100
200
300
400
CUMULATIVE VOLUME (l)

Figure 2

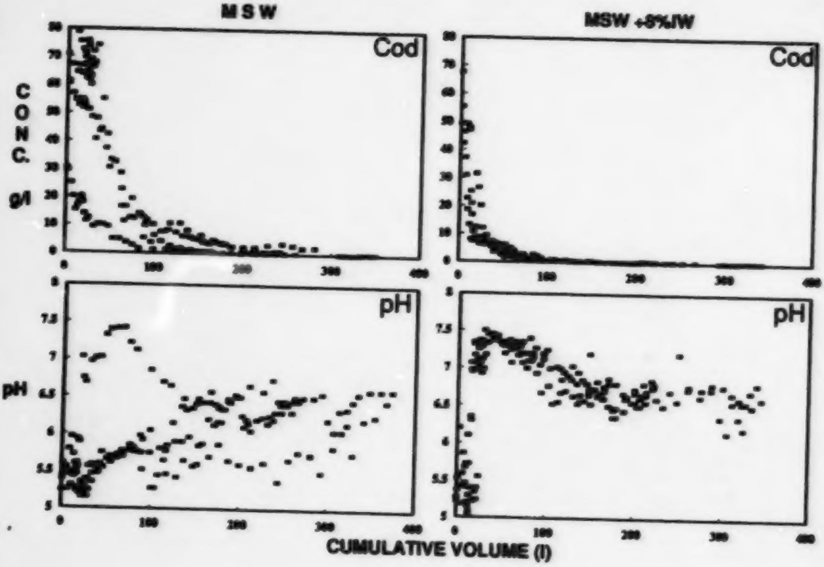
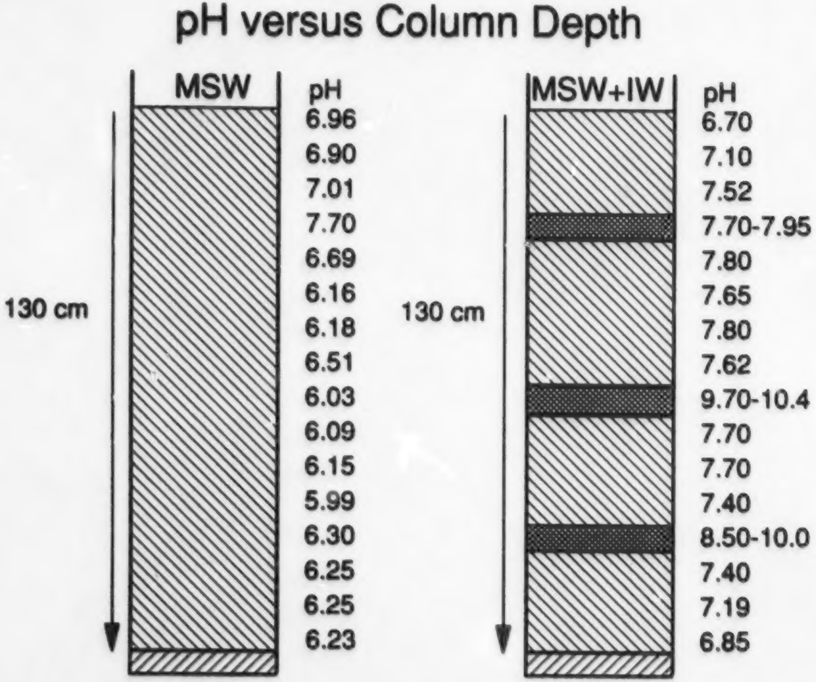

MSW
MSW +5%IW
Cod
Cod
C
O
N
C.
g/l
pH
pH
pH
0
10
20
30
40
50
60
70
80
5
5.5
6
6.5
7
7.5
8
0
100
200
300
400
CUMULATIVE VOLUME (l)

Figure 3



pH versus Column Depth

MSW
pH
6.96
6.90
7.01
7.70
6.69
6.16
6.18
6.51
6.03
6.09
6.15
5.99
6.30
6.25
6.25
6.23
130 cm
MSW+IW
pH
6.70
7.10
7.52
7.70-7.95
7.80
7.65
7.80
7.62
9.70-10.4
7.70
7.70
7.40
8.50-10.0
7.40
7.19
6.85
130 cm

Figure 4

Physical Modelling of Contaminant Plumes from Landfills

by R.J. Mitchell, Queen's University, Kingston, K7L 3N6

ABSTRACT

This paper considers physical modelling of landfill systems as an independent design approach. A dimensional analysis of the factors controlling contaminant transport in porous media is summarised and it is shown that gravitational modelling is necessary when carrying out physical modelling of transport in partly saturated soils. Centrifuge modelling has the added advantage of accelerating flow and transport phenomenon so that several years of real life (prototype) contaminant migration can be observed within days in the model. A 0.5m radius geotechnical centrifuge has been constructed specifically for modelling clay liner performance. Current research work, which includes liner leakage modelling and the transport of soluable contaminants in partly saturated soils, is outlined in the paper. Application of the modelling of models technique is discussed as a method of studying plume formations in cases where the centrifuge does not model all aspects simultaneously.

INTRODUCTION: CENTRIFUGE MODELLING IN GEOENVIRONMENTAL ENGINEERING

It is important, not only for an historic perspective but also to understand the potential application, to distinguish between centrifuge testing and centrifuge modelling. Bench centrifuges have been used, more or less continuously, for the past half-century to determine physical properties of materials, including hydraulic properties of porous media (see, for examples, Gardner, 1937; Russell and Richards, 1938). This is centrifuge testing and, like any other laboratory bench testing, is carried out to obtain input data for analytical solutions to (or numerical models of) field scale engineering problems. Centrifuge modelling was also introduced fifty years ago but has been redeveloped during the past 20 years, mainly for geotechnical applications (see, for examples, Schofield, 1978; Schofield, 1981). Real materials and boundary conditions are used to create a scaled physical model from which model behavioural phenomenon are observed. These physical observations are projected to the field (prototype) scale using analytical scaling relations. It is not necessary to know any material properties to carry out centrifuge modelling. Centrifuge modelling provides a completely independent solution to an engineering problem.

It is only within the past five years that centrifuge modelling has been applied to geoenvironmental problems such as contaminant transport (Arulanandan et al., 1988; Gronow et al., 1988; Cooke and Mitchell, 1991). This delay in the development of centrifuge modelling is due to the fact the large machines are needed to centrifuge large models. The centrifuge radius should be at least 10 times the model height to produce a suitably uniform acceleration field (Schofield, 1978). It is becoming apparent, however, that there are certain geotechnical/geoenvironmental problems for which centrifuge physical modelling is very well suited and may be considered state-of-the-art (Mitchell, 1990). Contaminant transport in partly saturated soils is certainly one such problem. The two purposes of centrifuge modelling in this area are (1) to examine transport phenomenon under modelled field conditions in order to predict field behaviour and (2) to produce complete "data sets" for idealized prototype situations to be used for validation of numerical models. At this stage of the development, both purposes appear to be equally important. At the present time, Queen's University Centrifuge Modelling Laboratory has two centrifuges: a 3m radius machine which, after six years of geotechnical stability modelling, has been converted for geoenvironmental modelling use and is dubbed "the green machine"; a 0.5m radius machine, designed and built in 1990 for clay liner modelling, which can be taken to field sites for liner permeability control testing, called, appropriately, "the mobile modeller".

CENTRIFUGE OPERATION AND SCALING FACTORS

Figure 1 is a schematic drawing of the green machine in its present form. A model is placed in the strongbox and balance masses are placed on the other end of the radius arm. When the machine is rotating at a constant angular velocity, ω, the model experiences an in-flight radial acceleration of $a = r\omega^2$. This acceleration acts on each and every atom in the model creating body forces which are similar to earth's gravitational forces. These body forces induce a stress distribution in the model. Thus, the first major advantage of centrifuge modelling is realized: when the model is constructed of prototype materials, under prototype densities and prototype boundary conditions, to a scale of N, and the model is in-flight at $a = Ng$,the stress distribution in the model will be similar to that of the prototype. Therefore, processes which are gravity driven, such as fracture and flow in earth materials, can be simulated in the physical model. Stress gradients will be increased N-fold in the model because two similar stress points will be closer in the model by the linear factor N. Thus, flow velocities will be increased as:

$$v_m = N\ v_p \qquad (1)$$

where the subscripts m and p apply to model and prototype, respectively, The distance a molecule flows between similar stress points will also be reduced by the linear scale, N, such that the time required for a flow process to occur is N^2 times faster in the model than in the prototype field situation. Then:

$$t_p = N^2\ t_m \qquad (2)$$

and the second major advantage of accelerated modelling is realised: ten years of field hydrodynamic phenomena can be simulated in 10 hours at a = 100g or in 10 days at a = 50g. These are appropriate scales for producing idealized data sets.

CENTRIFUGE MODEL SIMILITUDE

Physical modelling has been used for centuries to study physical phenomenon and it has been widely demonstrated that similar behaviour, in model and prototype, is observed when dimensionless mathematical expressions of similitude are fulfilled. For flow and contaminant transport, these conditions of similitude have been derived, published and discussed by Arulanandan et al. (1988) and by Cooke (1991). The two hydrodynamic expressions which are not similar are the Reynolds number and the Peclett number but Bear (1972)has shown that flow velocities are sufficiently small in fine grained soils that both of these numbers are less than unity. Darcy flow and molecular diffusion then control the advective-dispersive transport phenomenon and the lack of similarity in the hydrodynamic expressions does not affect the processes. It is of interest to note that molecular diffusion and other phenomenon are expected to be similar in centrifuge modelling of prototype transport situations such that plume shapes for real or idealized situations can be produced from centrifuge modelling. The two chemical expressions which Cooke (1991) defines as being dissimilar result because the chemical process involved (absorption and other reactions) require finite times to develop fully. In the faster model flow regime, these reactions may only be partially realized. Centrifuge modellers have, of course, developed a procedure for examining this problem—by carrying out model studies at different scales, a process referred to as modelling of models, real time effects may be discovered. In the present work a conservative contaminant (chloride tracer) was used to avoid chemical dissimilarities. The most important dimensionless expression for control of modelling in partly saturated soils is the capillary effects number (CEN) which is given by

$$CEN = \rho g\ Ll/T \qquad (3)$$

Where ρ is fluid density, g is the gravitational constant, L and l are characteristic macroscopic and microscopic lengths and T is the fluid surface tension. It is clear that $CEN_m = CEN_p$ only when the model is accelerated to $a = Ng$ so that $aL_m = gL_p$. Centrifuge modelling is essentially the only way to produce model similarily in the moisture-suction profile, hence in the advection -dispersion phenomenon, for a partly saturated prototype soil profile. This is the basic reason that centrifuge modelling must be considered state-of-the-art for studying flow and contaminant transport problems in partly saturated soils.

MODELLING OF LANDFILL PLUMES

Consider the potential for groundwater contamination from the typical lined landfill facility shown on Figure 2. Contaminants are prevented, or at least retarded, from reaching the ground water table by two barriers: the clay liner retards both advective and dispersive transport; the partly saturated soil provides both contaminant movement retardation and a contaminant holding capacity should breakthrough of the liner occur. Although it is possible to build a physical model of the complete prototype facility, it is more convenient to consider each barrier separately.

CLAY LINER MODELLING

Clay liners have been studied in considerable detail (see, for examples, Chapuis, 1990 ; Quigley, 1990) and it is known that good quality laboratory bench testing can provide accurate material property evaluations for clay liner design. However, laboratory bench testing is subject to equipment leakage and the compatibility of a given clay liner to organic leachates will depend on the effective stress in that liner. Centrifuges can be used in two ways to evaluate liner performance: (1) the centrifuge can be used as a materials testing machine to evaluate hydraulic conductivity and compatibility under prototype effective stress conditions and (2) centrifuge modelling of the liner-waste-leachate system can be carried out to directly determine the prototype leakage and contaminant migration. The current work in these areas is briefly outlined below.

Clay liners are generally in the order of 1m to 2m in thickness. A model scale in the order of 40 or 50 is a convenient scale for liner modelling because flow velocities would always be sufficient to provide results in one day of modelling but would be low enough so that the Reynolds and Peclett numbers would always be much less than unity. Thus, a model liner thickness in the order of 50mm would be sufficient for routine work and, hence, a centrifuge of 0.5m radius would be able to carry out this work. A centrifuge of this size is both inexpensive and portable and the 0.5m Mobile Modeller, shown on Figure 3, was designed and built at Queen's University to carry out liner modelling and testing. Figure 4 shows the liner modelling apparatus. The 76mm diameter liner model is sealed in the lower chamber by a silicon oil lateral pressure cell and has a porous plastic plate on the lower side to conduct any water and/or contaminant flow into the model lysimeter threaded into the base plate. The model landfill materials (sand cushion, leachate, etc.) are placed in the upper chamber. Both liner leakage and liner compatibility are modelled when prototype materials are used.

Liner permeability testing is carried out by confining the liner sample in the lower chamber and connecting saturated small diameter tubing to the water and silicon oil supply reservoirs located near the centre of rotation of the machine as shown on Figure 3. The water pressure on the top of the liner sample is calculated by simple integration of the pressure along the water supply tube and, hence, the hydraulic gradient across the liner sample is known at any centrifuge acceleration level. The confining pressure in the lateral pressure cell is maintained at an appropriate level (usually 5 to 10 kPa) above the sample top water pressure by an air pressure bag contained in the central section of the centrifuge arm (the air pressure acts on the top of the silicon oil reservoirs). To date, two series of liner permeability tests have been carried out. These test series indicate that centrifuge testing of the permeability of clay liners provides results that are accurate and that are obtained in less than 24 hours. A comparison of permeability data for 12 centrifuge and 12 bench tests caried out on consolidated specimens of Kaolin clay are presented in Table 1 and the following general conclusion has been drawn from this testing: centrifuge testing is an efficient method of determining clay permeability and problems of leakage or hydraulic fracturing are eliminated by this test method. Of equal or greater import to future clay liner design is the fact that centrifuge modelling can reproduce the field effective stress distribution through the liner. Effective stress is known to affect the ability of clay liners to resist detrimental interactions with organic leachates (see, for example, Quigley and Fernandez, 1989). Thus, centrifuge modelling can examine clay/leachate compatibility by reproducing field conditions in the laboratory. This work is currently underway at Queen's University Centrifuge Modelling Laboratory. The 0.5m radius Mobile Modeller can also be used for field control testing of liner samples, both for leakage and for leachate compatibility.

MODELLING OF TRANSPORT IN NATURAL SOILS

As noted earlier in this paper, centrifuge modelling is the necessary and sufficient condition for physical modelling of the movement of a conservative contaminant in a partly saturated fine grained soil. Indeed, the requirement that both the Reynolds number and the Peclet number be less than unity will hold for all soils with mean diameters up to about 0.5mm. The great advantage, of course, is that accelerated modelling will provide enormous real time advantages while maintaining similarity of all stresses. To date, the research on contaminant transport has been restricted to studying the one-dimensional movement of a chloride tracer in a partly saturated silty soil which is laboratory prepared in a sectioned soil column. Figure 5 shows the strongbox apparatus used for drainage, flow and contaminant transport modelling. The soil column is made up of up to 15 separate clear plastic rings of 75mm diameter and equipped with 'O'-ring seals to provide a water tight hollow cylinder into which the soil is placed at the required density. The upper and lower water tanks are designed to deliver water to, or accept water from, the top and base of the soil column at constant heads while monitoring these flow volumes to an accuracy of ± 2 cc. This constant head flow monitoring system is described in detail by Mitchell and Cooke (1991). The contaminant source container is designed to deliver up to 20 cc of a contaminant to the surface of the in-flight model. The general modelling sequence is as follows: (1) prepare the soil model in the column, (2) mount the soil column and flow control system in the centrifuge strongbox, (3) run the centrifuge at the selected acceleration ($a = Ng$) for a predetermined time to establish the desired moisture content profile, (4) introduce the contaminant at the central point on the soil surface while the centrifuge is running, (5) continue running the centrifuge for a selected time period, (6) stop centrifuge and section soil column to obtain contaminant distribution. Salt contents were measured by calibrated conductivity testing on each 20mm layer of soil.

The selected sequence was repeated using a new soil sample each time and the results were found to be consistent. These modelling runs were carried out at scales of 50 and 100. Figure 6 shows a typical result from the chloride tracer transport modelling. The data is dimensionalized by plotting the commulative salt to a given depth divided by the total salt added. Dimensionalizing the average salt contents accounts for the difference in the size of the salt plumes in the 50 scale and 100 scale models and provides a direct comparison of the results. All models represent a 2000 litre prototype surface spill of a 10% Na Cl solution (16 cc for 50 scale and 2 cc for 100 scale models, respectively) and these models were infiltrated for 6 hours and 9 hours (at 50 gravities) and 1.5 and 2.25 hours (at 100 gravities), respectively. The close agreement between the 50 scale and 100 scale results provides a high level of confidence in accepting the centrifuge modelling technique as an independent alternative for predicting prototype contaminant movements. Indeed, the numerical modelling alternative, in the case of contaminant movements in partly saturated soils, is at a very early stage of development. One of the future uses of centrifuge data sets will be to calibrate and/or validate numerical models. The test sequence which produced the data on Figure 6 is representative of a prototype contaminant spill rather than a steady state leakage through a clay liner. This modelling never-the-less demonstrates the principle and equipment has now been developed and calibrated for delivering contaminants to the soil surface at predetermined rates. Current research is being carried out to study plume migration (both in the vertical and the lateral directions) under steady leakage conditions and at larger model scales. There is no doubt that centrifuge modelling can contribute significantly to both the basic understanding and the predictive capabilities of contaminant transport in earth materials. Producing quality modelling data is, of course, a time consuming activity and there is still much development work to be done, particularly with regard to model sequence control and the in-flight monitoring of contaminant spreading.

CONCLUSIONS

Research carried out on the 0.5m Mobile Modeller centrifuge indicates that this machine is capable of producing quality liner permeability data for design (in the laboratory) and for construction control (in the field). The major advantages of the centrifuge method, over standard laboratory and field methods, is that rapid results can be produced without risk of apparatus leakage error and that the real (prototype) effective stress distribution can be reproduced in centrifuge models. This latter advantage is currently being exploited to study liner/leachate compatibility. Research carried out on the 3m radius Green Machine has established that the transport of a conservative contaminant through a partly saturated fine grained soil may be accurately represented by centrifuge modelling. Current and future research on this machine has been planned to improve modelling techniques, improve in-flight monitoring capabilities and to produce quality contaminant movement data sets under a variety of conditions and using several types of contaminants.

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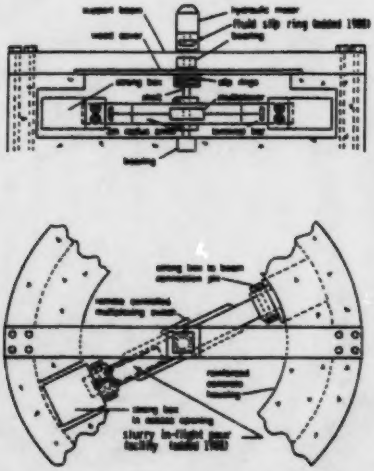
	BENCH TEST			CENTRIFUGE TEST	
Sample No	Saturated density g/cc	test time min.	hydraulic conductivity m/s X 10^{-9}	test time min.	hydraulic conductivity m/s X 10^{-9}
1	1.91	480	1.12	240	1.13
2	1.90	480	1.05	240	1.14
3	1.95	420	0.96	180	1.06
4	1.87	420	1.27	180	1.27
5	1.90	420	1.27	180	1.37
6	1.86	420	1.18	180	1.19
7	1.87	450	1.21	240	1.30
8	1.92	450	1.10	240	1.21
9	1.88	1100	1.28	180	1.23
10	1.94	1100	1.11	180	1.12
11	1.86	465	1.15	180	1.24
12	1.89	465	1.15	180	1.11

Table 1 - Comparison of Bench and Centrifuge Permeability Tests


hydraulic motor
bearing
slip rings
shaft
bearing

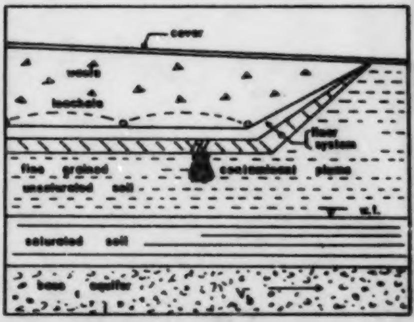

cover
waste
leachate
liner system
fine grained unsaturated soil
contaminant plume
w.t.
saturated soil
base aquifer
V_b

Figure 2 Typical Landfill

Figure 1 Queen's University 3m Radius Centrifuge

Figure 3 Mobile Modeller

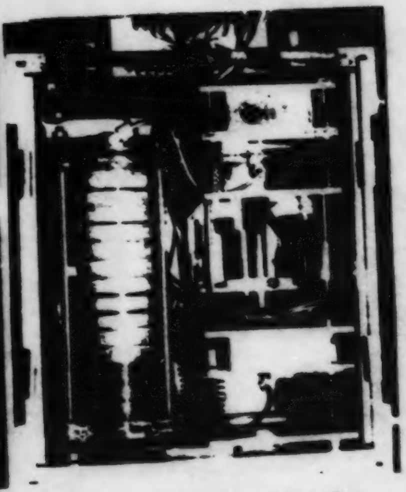


Figure 5 Strongbox Apparatus

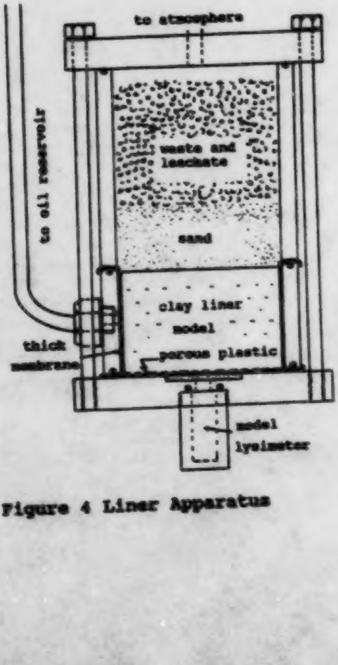

to atmosphere
to oil reservoir
waste and leachate
sand
clay liner model
porous plastic
thick membrane
model lysimeter

Figure 4 Liner Apparatus

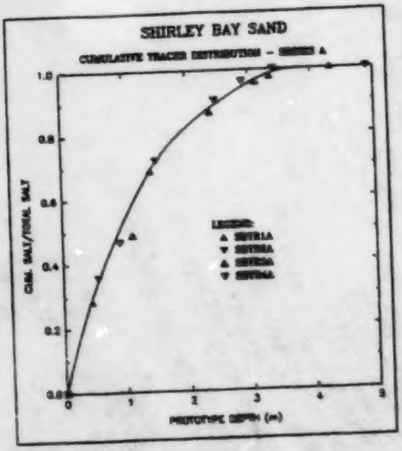


Figure 6

Typical Chloride Tracer Results

EXPERIMENTS ON DISSOLUTION OF TRICHLOROETHYLENE IMMOBILIZED IN SAND.

Philippe Lamarche*, G.J. Farquhar and J.F. Sykes, Department of Civil Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1.

Abstract

Many chlorinated solvents, although immiscible with water, are sufficiently soluble to create water quality hazards. When spilled into soil, solvents remain as discontinuous residuals within the pores from which dissolution will occur into adjacent ground water. Very little is known about the rates at which dissolution occurs or the factors which affect it. This is of particular interest with regard to the aqueous phase concentrations produced and the time required to reach non-hazardous conditions.

Experiments were performed on a laboratory scale to investigate the process of solvent dissolution in ground water. Trichloroethylene (TCE) was placed at apparent residual saturation in glass columns packed with different sands. One column contained chlorobenzene (CLB) instead of TCE. The TCE was dyed to allow visual observation of the contaminated sand zone. Water was pumped through the columns for one or two months, with flow rate and effluent TCE concentrations being monitored. Concentrations of TCE exceeding the recommended drinking water standards (5 $\mu g/L$) were measured until the end of the runs.

Solubility limit value (near 1400 mg/L) effluent concentrations of TCE were measured after 30 pore volumes of water in a mixed sand column. Effluent TCE concentrations then dropped below 10 mg/L in approximately 30 pore volumes. By that time, over 95% of the TCE had disappeared from the mixed sand column. The results for most other columns were similar.

When concentrations started decreasing, a short zone of sand containing dyed TCE could still be observed in all columns. This zone had disappeared by the time concentrations were below 10 mg/L. The TCE concentrations then decreased at a slower rate, such that concentrations over 400 $\mu g/L$, at a specific discharge of 1 m/d, were still observed after 220 pore volumes of water had passed through the mixed sand column. These concentrations are much higher than the recommended drinking water standard of 5 $\mu g/L$. The concentrations of TCE, after dropping below equilibrium (saturation) levels, were also observed to be inversely proportional to the specific discharge rate.

These and other experiments allowed investigation in greater detail of some of the factors affecting solvent dissolution in ground water. The experimental data was also reproduced with a finite element code solving the conservation of mass equations. A new conceptual model permitting better explanations of the laboratory observations was suggested.

0.1 Introduction

At the present, organic chemicals are the most commonly found hazardous contaminants in ground water (Mackay and Cherry, 1989). Many of these chemicals are immiscible with water (in water, they remain as separate, nonaqueous phase liquids or NAPL), but are sufficiently soluble in water to yield aqueous chemical concentrations above the drinking water standard for the chemicals considered. For instance, trichloroethylene (TCE; density 1.464 g/mL) has a drinking water standard of 5 $\mu g/L$ (Feenstra and Cherry, 1988) and an aqueous solubility of 1470 mg/L (Banerjee *et al.*, 1980).

When a DNAPL (an NAPL denser than water) is spilled in important quantity in the ground, its physical properties (high density, low solubility, and often low viscosity) allow it to penetrate deeply in the water saturated zone. The DNAPL may eventually become immobilised in the water saturated as well as in the vadose zone, in the form of disconnected ganglia dispersed through the soil column and of pools resting on less permeable strata. The migration and immobilisation of NAPL in the subsurface are complicated phenomena, and were studied by other authors (*e.g.*, Chatzis *et al.*, 1983; Morrow and Songkran, 1981; Schwille, 1988; Sitar *et al.*, 1987; Wilson and Conrad, 1984).

The fate of the DNAPL immobilised in a water saturated zone was of concern in this study. If the solubility of many DNAPL is high relative to their drinking water standard, it is relatively low compared to the amounts spilled in the environment. One litre of TCE could contaminate approximately 1000 litres of water at solubility limit, or approximately 3 × 10^8 litres of water at drinking water standard level. This illustrates the potential that a small DNAPL amount has to contaminate large volumes of ground water.

The concentrations of DNAPL in water, that determine the persistence and hazards of the contamination source, depend not only on the configuration of the DNAPL zones in the ground but also on the kinetics of dissolution. A knowledge of the effect on dissolution kinetics of various parameters (soil pore structure, ground water velocity, amount of NAPL entrapped) would also allow for a better design of remedial measures.

Table 0.1: Column Characteristics.

Column	Diameter (cm)	Sand	Length[b] (cm)	DNAPL Length (cm)	DNAPL Volume (mL)	DNAPL Residual saturation	Pore velocity (cm/h)
1-P	2.7	#20-30	19	8.5	2.1	0.119	9.79–11.32
1-D	2.7	#20-30	19	8.5	2.3	0.130	9.89–10.61
2-M	5.1	Mixed	31.8	10.0	12.5	0.186	0.75–14.60
2-U	5.1	#71	32.3	8.8	10.55	0.164	0.67–13.10
3-1	5.1	#20-30	32.9	10.8	11.8	0.157	4.64–5.55
3-2	5.1	Graded[a]	34.0	10.0	9.9	0.173	5.55–6.58
3-3	5.1	#71	34.1	11.5	12.65	0.166	4.73–5.70
3-4	5.1	#71	32.5	10.6	10.05[c]	0.131	11.41–12.55

a) Well graded mixed sand.

b) Length of sand zone, including sand above plunger-type screen.

c) Approximate volume only, one measurement not recorded.

0.2 Literature Review

To date, a few experimental studies were published on the dissolution of NAPL in water flowing through porous media columns or troughs. Studies on multicomponent NAPL (*e.g.*, petroleum hydrocarbon mixtures) dissolution showed evidence of selective dissolution, *i.e.*,, dissolution and complete disappearance of the more soluble components from the mixture, each in turn, as dissolution proceeded (Bastien *et al.*, 1977; Fried *et al.*, 1979; Ramanantsoa *et al.*, 1986; Rimmelin *et al.*, 1986; Zilliox *et al.*, 1978); however, the detection limits of methods used to measure aqueous concentrations were often high (van der Waarden *et al.*, 1971; Zilliox *et al.*, 1973), preventing detection of trace amounts of the components that may have remained. Analytical methods used in some studies on single component residual (disconnected ganglia) NAPL dissolution had much lower detection limits. A finding of some studies was that equilibrium (solubility limit) aqueous concentrations prevailed for a period of time (Anderson, 1988; Imhoff *et al.*, 1990). However, the experimental conditions (water velocity, pore structure, and NAPL emplacement) were often not representative of those expected in the field (Geller and Hunt, 1989; Imhoff *et al.*, 1990; Miller *et al.*, 1990). Furthermore, none of the experiments presented were carried out until complete exhaustion of the NAPL source; the largest amount of source depletion reported was 86% (Schwille, 1988). And yet, some effects of kinetic limitation to the dissolution of NAPL could become apparent only when most of the NAPL has dissolved.

0.3 Objectives

It was therefore decided to experimentally investigate the dissolution of a single component residual DNAPL in water flowing through sand columns. The experiments were to be carried out until or as close as possible to exhaustion of the DNAPL source. Other factors investigated besides the DNAPL source exhaustion were the effect of ground water velocity and sand size distribution on dissolution kinetics. TCE was selected as the DNAPL, because it is one of the five most commonly found organic chemicals in ground water in the United States (Feenstra and Cherry, 1988) and had the desirable properties (relatively high solubility and low vapour pressure). One experiment (Column 3-4) was carried out with chlorobenzene (CLB) instead of TCE, to assess the effects of the chemical on the dissolution rate. The data were reproduced with a finite element code solving the conservation of mass equations, yielding mass transfer coefficients to be used when predicting DNAPL contamination severity and source life under natural as well as induced (*e.g.*, pump-and-treat remediation) conditions.

0.4 Experimental Procedure

The experiments were carried out in glass columns. Table 0.1 presents the main characteristics of the columns. Silica sands were used. Sand size distributions are presented in Figure 0.1; not shown is the #20-30 sand, that passed the No. 20 and was retained on No. 30 U.S. sieve. In the 2.7 cm dia. columns, the sand, supported by glass beads, was poured dry in the columns. In the 5.1 cm dia. columns, the sand was wetted (10% w/w with water), mixed and compacted in 1 cm layers; it was supported by a stainless steel screen and compressed against it by a plunger-type screen (Lamarche, 1991). The compressed sand zone length accounted for over 80% of the total sand zone length given in Table 0.1 (sand was added above the plunger-type screen to fill the column cap).

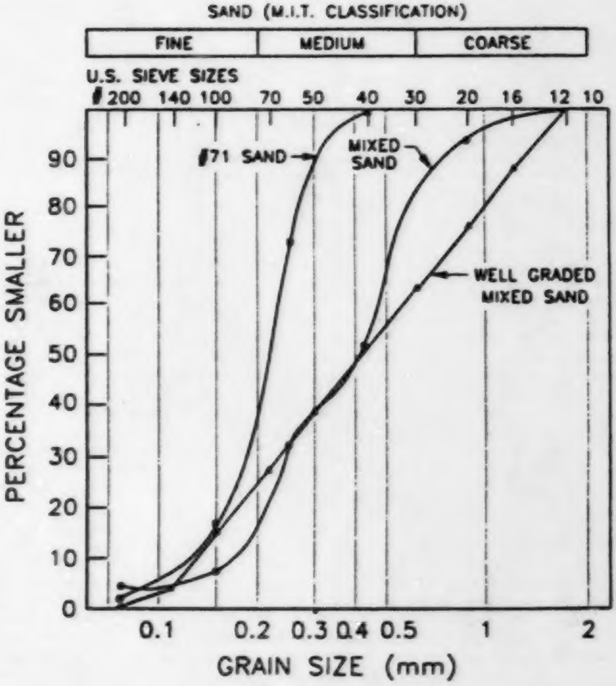


Figure 0.1: Sand Size Distribution Curve.

After packing, the columns were purged with CO_2, and flooded with degassed water (degassed by boiling and rapidly cooling). The DNAPL (TCE, CLB for Column 3-4) was forced up and then allowed to drain from the water saturated sand; the entrapped volume was recorded. Except for Column 1-P, the DNAPL was dyed red; the sand containing residual DNAPL appeared pink, in order to measure the length of contaminated sand zone and to compute the DNAPL residual saturation (Table 0.1).

Degassed water was pumped through the columns at pore velocities (Table 0.1) around the upper range of typical ground water velocities in uniform sand and gravel aquifers (11.4 *cm/h*, Mackay *et al.*, 1986). Flow rates and effluent aqueous DNAPL concentrations were monitored daily (or at longer regular intervals for the end of the experiment in Columns 1-P and 1-D). Flow rates were kept as close to constant as possible except in Columns 2-M and 2-U, in which they were varied.

0.5 Experimental Results and Discussion

The concentrations and velocities are plotted against time for Columns 2-M and 2-U in Figure 0.2. Note the exaggerated concentration scale necessary to show the low concentrations on the bottom graph. Some TCE was entrapped between the sand support plate and glass wall in Column 2-U and started dissolving only at 1315 *h*, approximately. Due to this TCE dissolving, the effluent concentrations of Column 2-U were not proportional to those of Column 2-M between 1315 and 1465 *h*. The Column 2-U "corrected" data were computed to reflect that proportionality (to the data of Column 2-M) observed before 1315 *h* and after 1465 *h*. The TCE around the support plate was probably also responsible for the slower rate of decrease of concentrations in Column 2-U, but that could not be accounted for with the available data.

The bottom graph of Figure 0.2 shows the inverse proportionality between concentration and velocity (*i.e.*, higher concentrations at lower velocities) that was expected for kinetically (as opposed to solubility) limited mass transfer. The relationship was not linear, however, and relatively more mass of solute came out of the columns at lower velocities. This observation could have an impact on source life computations and remediation schemes design.

The data of all experiments were normalized by dividing the effluent concentrations by the average maximum concentration for the respective experiment, and multiplying the time elapsed by the water flow rate and dividing by the void volume of the DNAPL contaminated sand zone to compute the number of pore volumes. The normalized data for all experiments are presented in Figure 0.3, on semi-logarithmic axes.

Figure 0.3 shows that all data sets exhibited the same general behaviour, that is, an initial period of high effluent concentrations followed by a sharp drop to low, slowly decreasing concentrations. The low concentrations were at least one hundred times smaller than the high concentrations.

The high concentrations ranged between 70 and 95% of solubility limit values found in the literature. This indicated that solubility limited mass transfer prevailed initially, and was in agreement with observations made by other authors (Anderson, 1988; Bastien *et al.*, 1977; Fried *et al.*, 1979; Miller *et al.*, 1990; Schwille, 1988; Zilliox *et al.*, 1973).

The long period of low, slowly decreasing concentrations was not discussed in the literature to date. Table 0.2 presents the amount of DNAPL removed at the beginning of the low concentration period (termed "plateau" in the table). Most experiments reported in the literature were interrupted before that period of low concentrations could even be observed (when 80% or less of the DNAPL source was exhausted). And yet the low concentration periods were observed in each experiment performed in this study. They were observed for 160 to 1631 pore volumes (Table 0.2), and were terminated only by interruption of the experiments. Effluent TCE concentrations at the end of the low concentration period were over forty times larger than the drinking water standard (Table 0.2).

The CLB was more difficult to quantify than TCE, and the mass balance calculation could be in error. However, the milder rate of sharp decrease in concentrations and larger amount remaining in Column 3-4 at the beginning of the low concentration period indicate that the chemical had an effect on the kinetics of dissolution.

The different sands used did not appear to have an important effect on the dissolution rates of TCE, however. The rate of sharp decrease in concentrations was similar for most TCE columns (Figure 0.3). The different rate observed in Column 2-U can be attributed to the TCE that was trapped around the sand support ring. Column 3-2 also exhibited a milder rate of decrease in concentrations for part of the sharp drop period, but that was probably caused by an isolated pocket of TCE that could be seen in the sand, against the glass wall, to dissolve slowly; that pocket extended only through part of the cross-section of the column. The pocket, just like the visible DNAPL in all columns, had completely vanished by the time the low concentration period started.

Evidence offered by the experiments described above and by complemental experiments (Lamarche, 1991) led to conclude that the long periods of low concentrations observed in each dissolution experiment were not caused by the DNAPL having been adsorbed and desorbing slowly or by it being present in the dissolved form in dead zones inside the column. The

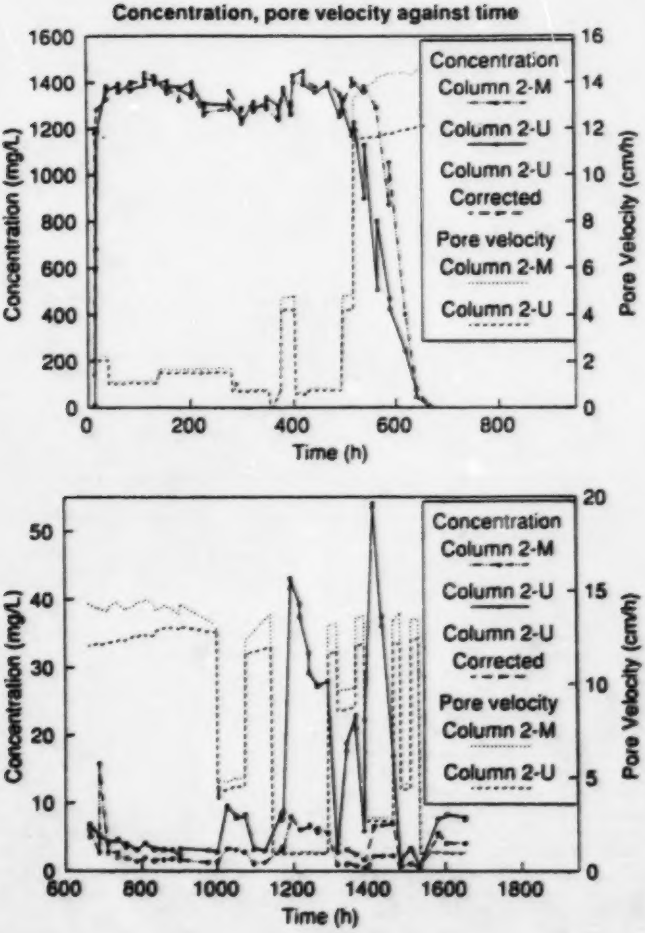


Figure 0.2: Effluent Concentration, Velocity, Against Time, Columns 2-M, 2-U.

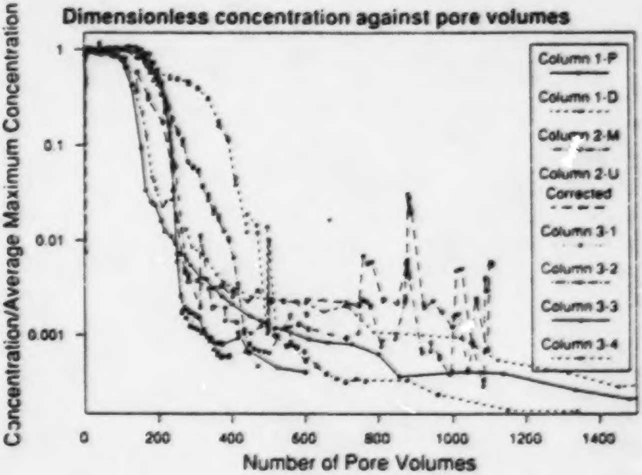


Figure 0.3: Normalised Concentration Against Pore Volumes, Semi-logarithmic Plot.

Table 0.2: Concentrations and Mass Balance.

Column	Plateau			Final	
	Pore volumes[a]	DNAPL removed[b]	Concentration[c] (mg/L)	Pore volumes[a]	Concentration[c] (mg/L)
1-P	612	0.917	1.2	2243	0.22
1-D	601	0.920	2.9	2192	0.21
2-M	280	0.973	5.1	1097	0.47[d]
2-U	272	0.827	6.3	1110	0.95[d]
3-1	286	0.900	1.4	470	0.58
3-2	433	0.875	1.2	692	0.59
3-3	271	0.909	2.0	661	0.44
3-4	523	0.616	0.34	1340	0.056

a) Number of contaminated zone pore volumes of water having flowed through the column.
b) Relative amount of DNAPL removed from the column.
c) Effluent aqueous DNAPL concentration.
d) Concentrations at the highest flow rate, near the end of the experiment.

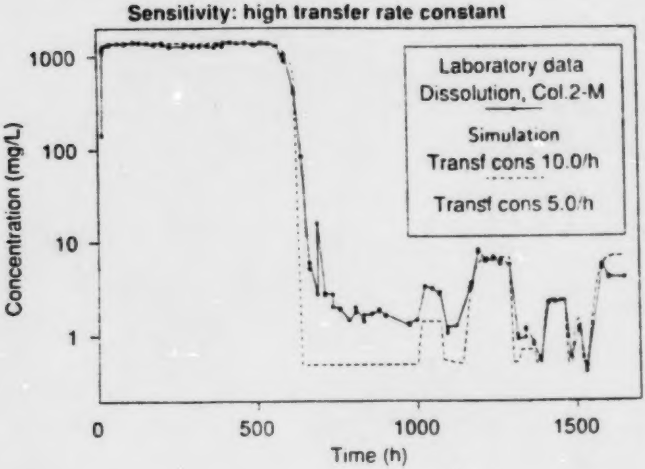


Figure 0.4: Data Simulation With Bicontinuum Model.

DNAPL, present as a separate phase, did not dissolve slowly due to accumulation of dye or impurities in it or to the presence of isolated pockets of DNAPL in the columns.

It was concluded that the long periods of low concentration resulted from the remaining portion of DNAPL being entrapped in low permeability zones in the sand (dead-end pores, or micro-aggregates; Moulijn and Van Swaaij, 1976; Volkov *et al.*, 1986). Dissolution and transport from these low permeability zones being slow, the result is low concentrations and a long source life.

0.6 Modeling

The general behaviour of the data could not be reproduced with a one-region model (normally used to describe dissolution; Miller *et al.*, 1990; Powers *et al.*, 1991), and a two-region (bicontinuum) model was required. In a bicontinuum model, the DNAPL mass is separated in two portions, one that dissolves rapidly and the other dissolving slowly. Figure 0.4 shows the results of simulations of the data of Column 2-M with the bicontinuum model.

If the general behaviour was reproduced with the bicontinuum model, there were still discrepancies. This observation led to the suggestion of a conceptual model that is believed to better represent the physics of dissolution of DNAPL in the soil. In this model, the soil is considered to consist of different pore categories (pores or groups of pores of different permeabilities) from which DNAPL dissolution proceeds at different rates. The model is thus not a bicontinuum model (two rates of dissolution only), but rather a "multicontinuum" model. The dissolution rate of residual DNAPL and its variation as dissolution proceeds then reflects the effect of the disappearance of DNAPL from some pore categories with time. This approach contrasts with that found in the literature so far, where the dissolution rate was assumed constant in time or correlated to the NAPL residual saturation (Miller *et al.*, 1990) without regard for the pore structure and DNAPL distribution. More details on the modeling can be found in Lamarche (1991).

0.7 Summary and Conclusions

The major findings of this study could be summarised as follows:

1. Equilibrium (solubility limit) concentrations initially resulted from the dissolution of residual DNAPL in water-saturated sand columns.
2. When most of the DNAPL source was exhausted, however, much lower, and slowly decreasing, concentrations were observed; a) these low concentrations were affected by the water flow rate (kinetically controlled mass transfer), b) the relationship of mass transfer to flow rate was not linear, and c) the concentrations were observed for long time periods.
3. Different chemicals had different dissolution rates.
4. Different sand size distributions apparently did not affect the rate of dissolution of TCE.
5. The multicontinuum conceptual model appears to better describe the physics of dissolution; however, a bicontinuum model allowed to reproduce the general behaviour of the data.

Practical consequences of these findings are:

a) A DNAPL spilled in the soil, even in homogeneous soil with no large scale heterogeneities, could provide a long term source of contamination.

b) the kinetics of dissolution should be taken into account when evaluating source life or designing remedial measures.

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A12

THE INFLUENCE OF pH AND CHLORIDE ON THE RETENTION OF ZINC, LEAD, CADMIUM AND MERCURY BY SOIL.

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ABSTRACT

A major problem resulting from the disposal of waste in landfill sites is the generation of large quantities of leachate which may move out of the fill and contaminate associated surface and ground waters with toxic metals. The charged surfaces of soil and sediment particles are able to form complexes with metallic cations and anions and thus can attenuate these toxic pollutants. The extent of attenuation is however very pH-dependent and, in addition, soluble complexant ligands, such as chloride, Cl^-, can compete with the charged surfaces for the small amounts of toxic metals in solution and thereby reduce their retention by soils and sediments. The objective of this study was to assess the influence of pH and Cl^- ions on metal retention in soil by quantifying the adsorption of Zn, Pb, Cd and Hg in the presence of a complexing ligand, Cl^-, and a non-complexing ligand, perchlorate, ClO_4^-. The results showed that at the pH where the relative proportion of total added metal retained in the presence of 0.1M perchlorate was 50%, the corresponding proportion retained from a 0.1M Cl^- solution was 48% for Zn, 40% for Pb, 22% for Cd and <5% for Hg. The relative effect of Cl^- ions on suppressing the retention of these metals was found to be proportional to the formation constants of their aqueous Cl^- complexes. The effect of pH and Cl^- ions on metal retention is currently being modelled using a number of surface complexation models. A major problem associated with this modelling is the lack of thermodynamic data for the surface complexation reactions.

INTRODUCTION

Landfill leachates often contain high concentrations of both toxic metals and complexant inorganic and organic ligands (Bolton and Evans, 1991). Of environmental concern is the possible movement of these metals from the landfill to surrounding soils and sediments. This movement may cause contamination of associated surface and ground waters. Organic and mineral particles contained within soils and sediments carry electrostatic charges and thus may attenuate these toxic metals by forming both inner- and outer-sphere complexes with charged metallic cations and anions (Evans, 1989). Metals in solution may exist as individual ions or as complexes with various inorganic and organic ligands. In order to ascertain the fate of a given metal in soils and sediments the speciation of the metal in solution must be known.

The formation of metal complexes in solution can affect the retention of metals in a number of different ways. Complexant ligands in solution that form strong complexes with the metal can compete with the surface complexes on soil and sediment particles. The magnitude of this effect will depend on both the formation constant of the aqueous metal-ligand species and the soil or sediment surface complexation constant for the metal. Clays with permanent negative charges are common constituents of soils and sediments and metallic cations form weak outer-sphere complexes with these clay surfaces. However metal-ligand complexation reactions may result in soluble complexes with neutral or even negative charges and these complexes would not be retained by clay surfaces. In addition, if a mineral phase controls the equilibrium solution concentration of the free metal then any complexation reactions will increase the total amount of metal in solution, i.e. the sum of the free metal plus the complexed metal species, will be increased. This mechanism may be responsible for increased metal concentration in solution when ligands are present that form strong complexes with the metal (Hahne and Kroontje, 1973).

Of direct relevance to metal mobility in landfills in Ontario is the observed increased mobility of metals due to complex formation when chloride levels are increased dramatically during disposal of large quantities chloride containing wastes, such as those from food processing wastes and road grits contaminated with residual road salt. Increased leaching of metals due to elevated concentrations of Cl^- ions has been noted previously (Doner, 1978).

This work reports on the role of pH on metal retention and on the influence of the complexant chloride ion, Cl^-, on the chemical speciation and retention by a soil of the four metals Zn, Pb, Cd and Hg. The effect of Cl^- on the adsorption of the metals by soil has been determined by comparing the extent of retention of the metal in the presence of Cl^- with that obtained in the presence of the non-complexing ligand perchlorate, ClO_4^-.

MATERIALS AND METHODS

Adsorption experiments

A soil sample from the Ap horizon of the Welland series (Orthic Humic Gleysol; Typic Humaquept) was air dried and ground to pass through a 2mm sieve. This soil had a clay content of 50%, an organic C content of 3% and an initial pH measured in 0.01M $CaCl_2$ of 4.23.

A suitable range of pH values was obtained by adding appropriate quantities of 1 M LiOH or 1 M $HClO_4$ to 50 ml centrifuge tubes containing 100 mg of soil in either 25 ml of 0.1 M LiCl or 0.1 M $LiClO_4$ solution. After equilibrating at 25°C for 8 days, aliquots of either Zn, Pb, Cd or Hg solutions were added to the tubes to obtain initial metal concentrations of 2.0 x 10^{-4} M for Zn and Cd and 3.0 x

10^{-4} M for Pb and Hg. These concentrations were chosen to minimize the possible precipitation of metal hydroxides or carbonates at higher pH values. The solutions were shaken at 25°C for a further 24 h, the tubes centrifuged and the solutions filtered through 45 μm filters. The content of metal remaining in solution was determined on a LECO PLASMARRAY ICP - AE spectrometer. A HACH free diffusion junction electrode was used to measure the pH on the remaining solution. The adsorption experiments were carried out in duplicate.

Metal speciation calculations

To estimate the relative proportions of soluble complexes of Zn, Pb, Cd and Hg as a function of pH and Cl^- ion concentration a simple metal equilibrium speciation model was written. The complexant inorganic ligands considered in the model were OH^-, Cl^-, HCO_3^- and CO_3^{2-}. The concentrations of HCO_3^- and CO_3^{2-} were calculated assuming an atmospheric partial pressure for CO_2 of 0.00032 atm. Calculations of the equilibrium chemical speciation of metals as a function of pH can be obtained from a knowledge of the total concentrations of all metals, $\{Me\}_T$, the total concentrations of complexant ligands, $\{L\}_T$, in solution and the equilibrium formation constants, β_{MeL}, of all complexes under consideration.

The complexation of a divalent metal, Me^{2+}, with a ligand, L^{f-}, to form a mononuclear complex, $MeL_n^{(2-n\cdot f)}$, where n is the number of complexant ligands, can be described by:-

$$Me^{2+} + nL^{f-} \rightleftarrows MeL_n^{(2-n\cdot f)} \qquad (1)$$

$$\beta_{MeL} = \frac{\{MeL_n\}}{\{Me\}\{L\}^n} \qquad (2)$$

Total metal, $\{Me\}_T$, in solution is thus considered to be made up of the free ionic form, Me^{2+}, plus the twelve complexed species and the mass balance is shown by the following equation:-

$$\begin{aligned}\{Me\}_T = {} & \{Me^{2+}\} + \{MeOH^+\} + \{Me(OH)_2^0\} + \{Me(OH)_3^-\} + \{Me(OH)_4^{2-}\} + \{MeCl^+\} + \\ & \{MeCl_2^0\} + \{MeCl_3^-\} + \{MeCl_4^{2-}\} + \{MeHCO_3^+\} + \{MeCO_3^0\} + \{Me(CO_3)_2^{2-}\} \qquad (3)\end{aligned}$$

By including all the relevant equilibrium formation constants, equation (3) can be rearranged to give:

$$\begin{aligned}\{Me\}_T = {} & Me^{2+}\,[1 + \frac{\beta_1}{\{H^+\}} + \frac{\beta_2}{\{H^+\}^2} + \frac{\beta_3}{\{H^+\}^3} + \frac{\beta_4}{\{H^+\}^4} + \beta_5\{Cl^-\} + \beta_6\{Cl^-\}^2 + \\ & \beta_7\{Cl^-\}^3 + \beta_8\{Cl^-\}^4 + \beta_9\{HCO_3^-\} + \beta_{10}\{CO_3^{2-}\} + \beta_{11}\{CO_3^{2-}\}^2]. \qquad (4)\end{aligned}$$

The contents of Cl^-, HCO_3^- and CO_3^{2-} can calculated from the following equations:

$$\{Cl\}_T = \{Cl^-\} + \beta_5\{Me^{2+}\}\{Cl^-\} + \beta_6\{Me^{2+}\}\{Cl^-\}^2 + \beta_7\{Me^{2+}\}\{Cl^-\}^3 + \beta_8\{Me^{2+}\}\{Cl^-\}^4 \qquad (5)$$

$$\{HCO\}_3^- = K_{a1}\,K_H\,pCO_{2(g)}/\{H^+\} \qquad (6)$$

$$\{CO_3^{2-}\} = K_{a1}\,K_{a2}\,K_H\,pCO_{2(g)}/\{H^+\}^2 \qquad (7)$$

where K_{a1} and K_{a2} are the dissociation constants for carbonic acid, K_H is the Henry's Law constant and pCO_2 is the partial pressure of carbon dioxide.

Table 1. Formation constants for the aqueous complexes of Zn, Pb, Cd and Hg†

	log β			
	Zn	Pb	Cd	Hg
$Me^{2+} + H_2O \rightleftarrows MeOH^+ + H^+$	-8.96	-7.71	-10.08	-3.40
$Me^{2+} + 2H_2O \rightleftarrows Me(OH)_2^{\circ} + 2H^+$	-16.90	-17.12	-20.35	-6.17
$Me^{2+} + 3H_2O \rightleftarrows Me(OH)_3^- + 3H^+$	-28.40	-28.06	-33.30	-21.10
$Me^{2+} + 4H_2O \rightleftarrows Me(OH)_4^{2-} + 4H^+$	-41.20	-	-47.35	-
$Me^{2+} + Cl^- \rightleftarrows MeCl^+$	0.49	1.58	1.97	7.43
$Me^{2+} + 2Cl^- \rightleftarrows MeCl_2^{\circ}$	0.62	1.82	2.59	14.25
$Me^{2+} + 3Cl^- \rightleftarrows MeCl_3^-$	0.51	1.71	2.40	14.46
$Me^{2+} + 4Cl^- \rightleftarrows MeCl_4^{2-}$	0.20	1.40	1.47	15.27
$Me^{2+} + HCO_3^- \rightleftarrows MeHCO_3^+$	-	3.45	2.10	5.82
$Me^{2+} + CO_3^{2-} \rightleftarrows MeCO_3^{\circ}$	4.75	6.27	4.12	12.10
$Me^{2+} + 2CO_3^{2-} \rightleftarrows Me(CO_3)_2^{2-}$	-	9.49	-	15.62

† Values taken from Turner *et al.* (1981) and Gunneriusson and Sjöberg (1991)

RESULTS AND DISCUSSION

The relative proportion of added Zn, Pb, Cd and Hg adsorbed in the presence of 0.1 M solutions of complex forming Cl^- ions and non-complex forming ClO_4^- ions for a range of pH values are shown in Figures 1a, b, c and d. The 0.1 M Cl^- ion concentration chosen for the study is comparable with Cl^- ion concentrations found in local landfill leachates with a Cl^- ion concentration of 0.07M having been reported for the Guelph landfill leachate (Bolton and Evans, 1991).

The results reported here indicate that the proportion of metal adsorbed increases to a maximum with increasing pH. In the ClO_4^- ion electrolyte the pH at which the relative proportion of adsorbed metal reached 50% increased in the order Hg, Pb, Zn, Cd. This order corresponded to the increase in the value of the hydrolysis constants for the formation of the aqueous $MeOH^+$ species. This relationship between the tendency of a metal to adsorb onto a particle surface and its ability to hydrolyse in water has been noted previously by Schindler and Stumm (1987). The results of the adsorption experiments in the presence of Cl^- ions showed that the decrease in metal adsorption relative to that in the ClO_4^- solution increased in the order Zn < Pb < Cd < Hg. The effect was most pronounced for Hg with there being virtually no adsorption in the presence of Cl^- ions for values of pH less than 7.0. The effect of Cl^- ions on metal retention is directly related to the ability of the metals to form soluble complexes with Cl^- ions.

The equilibrium formation constants of the various metal species used to construct the various speciation diagrams are shown in Table 1. The relative proportion, α_i, of each species MeL_n is then defined as $\{MeL_n\}/\{Me\}_T$, for example, $\alpha_{CdCl} = \{CdCl^+\}/\{Cd\}_T$. Results from the calculations on the chemical speciation of the metals showed that speciation is greatly influenced by presence of Cl^- ions (Figures 2 and 3). In the presence of 0.1M Cl^- the proportion of non-complexed Zn^{2+}, for example, is 74%, whereas for Cd^{2+} it is 7%. Similarly, for Cd the neutrally charged species $CdCl_2^{\circ}$ constituted 27% of $\{Cd\}_T$ over a large part of the pH range. Calculation on the speciation of Hg revealed that in the presence of Cl^- ions for the pH range 3-7, 80% of the Hg was present as the neutrally charged $HgCl_2^0$, and that significant proportions of negatively charged $HgCl_3^-$ and $HgCl_4^{2-}$ species were also present.

The results of this study suggest that high concentrations of Cl^- ions in solution can decrease the retention of metals such as Pb, Cd and Hg by soil. These results are in contrast to those for Zn where very little difference in metal retention was observed at high Cl^- ion concentrations. The results suggest caution in the disposal of large amounts of NaCl containing wastes, such as salt contaminated road grits and food processing wastes. Further studies are required to determine the surface complexation constants of metals with soils and sediments to improve prediction of metal retention and to investigate further the effects of other complexant ligands commonly found in landfill leachates.

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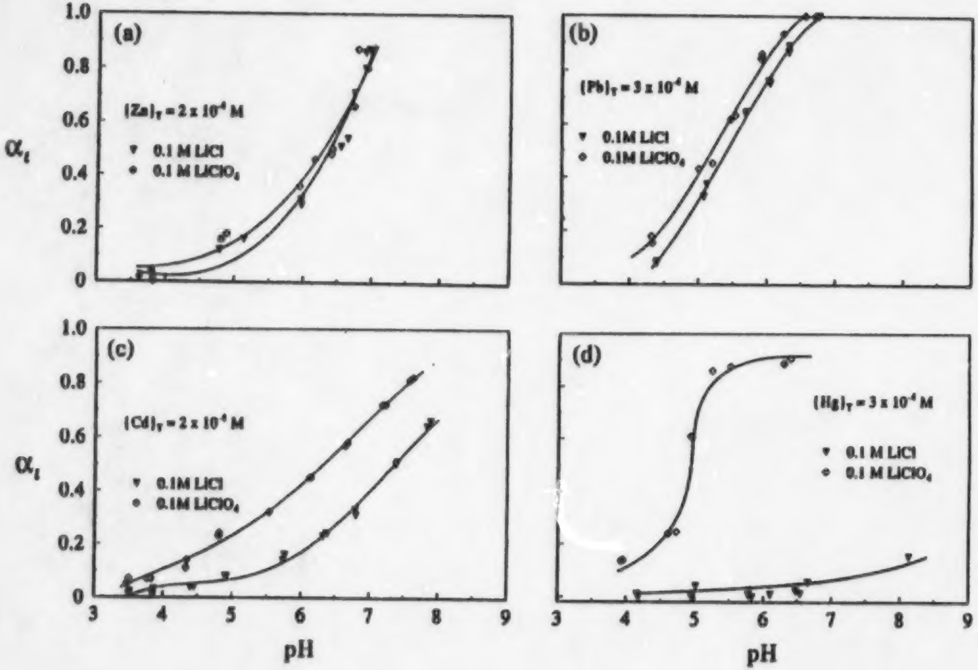

Figure 1. Adsorption of (a) Zn, (b) Pb, (c) Cd and (d) Hg onto soil as a function of pH in the presence of 0.1M LiCl and 0.1M LiClO$_4$.

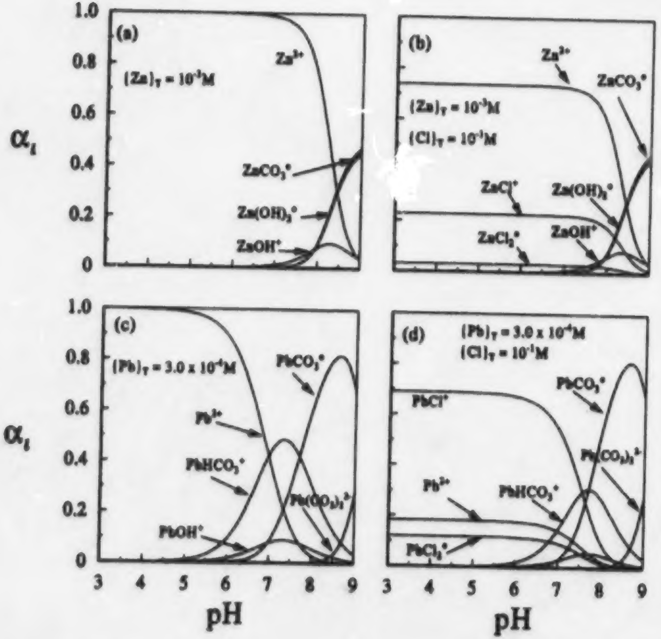

Figure 2. Speciation of Zn (a and b) and Pb (c and d), respectively, in the presence and absence of 0.1 M Cl^{-} solution.

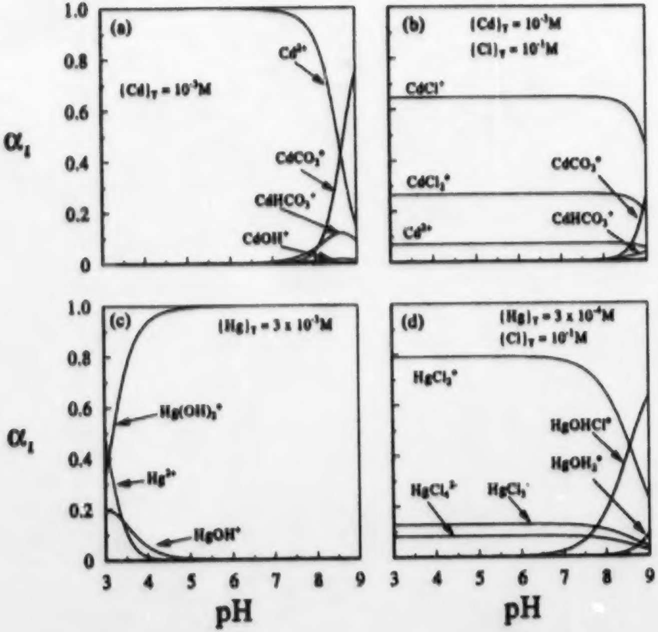

Figure 3. Speciation of Cd (a and b) and Hg (c and d), respectively, in the presence and absence of 0.1 M Cl^- solution.

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CHEMICAL EXPOSURE PATHWAYS IN ONTARIO

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Introduction

It is alleged that there are some 60,000 chemicals in current commercial production, with approximately 1000 being added each year. Of these, perhaps 500 are of environmental concern in Ontario because of their presence in detectable quantities in various components of the Great Lakes Ecosystem, their toxicity, their tendency to bioaccumulate, or their persistence. A view is emerging that some of these chemicals are of such extreme environmental concern that all production and use should cease, i.e. as a global society we should elect not to synthesise or use them. They should be "sunsetted". PCBs, "dioxins" and freons are examples. A second group consists of chemicals which are of concern because they are used or discharged in large quantities, or they are unusually toxic or persistent. They are, however, of sufficient value to society that their continued use is justified, but only if we fully understand and control their sources, environmental fate, the exposure experienced by organisms, including humans, and ultimately their effects. This understanding is essential if society is to be assured that there are no adverse ecological or human health effects. Other less harmful chemicals can be treated with less rigor.

If we accept this "cradle to grave" approach, we must improve our skills in assessing chemical fate in the environment. We must improve our understanding of chemical sources, how they migrate in and between the various media of air, water, soils, sediments and their biota which comprise our biosphere. We must understand how these chemicals are transformed by chemical and biochemical processes and thus how long they will persist in the environment. We must understand how, and to what extent, organisms become exposed to these chemicals and ultimately the nature of the effects which they may have on the multitude of interacting organisms which occupy these media, including ourselves.

It is now clear that the fate of chemicals in the environment is controlled by a combination of two groups of factors. First are the conditions prevailing in the environment such as temperature, flows of air, water and solid matter and the composition of these environmental media. Second are the properties of the chemicals which influence partitioning and reaction tendencies, and determine the environmental behavior of the chemical, such as evaporation or association with sediments, and possible destruction by conversion to other chemical species. These factors combine to control concentration in various environmental media, especially the "human exposure media" of air, water, fish, vegetation and domestic animals which comprise our diet.

During the last few years we have been working with Ministry support to develop models of chemical fate and exposure. Some results of this effort have been published recently (Mackay and Paterson 1991), thus in this report we focus on one aspect of this on-going effort, namely the development of a generic environmental fate and exposure model which can be applied to Ontario and to other jurisdictions. The model has been designed to be very simple, robust, and readily adaptable to other regions.

Environmental Fate Calculations

We believe that the preferred approach is to conduct three calculations of increasing complexity, namely Level I, II and III fugacity evaluations. Only a brief review is presented here.

In the generic model the region selected has an area of 100,000 km^2 which is about half the area of Southern Ontario, with 10% water, 90% soil and an atmosphere extending to a height of 1000 m. These volumes and areas and the composition of the soil and sediment can be readily varied.

The Level I calculation describes the partitioning at equilibrium of a given amount of chemical (typically 100000 kg or 100 tonnes) between six media of defined volumes, namely air, water, soil, bottom sediment, suspended sediment and fish. Table 1 summarises the media dimensions, Z values and the environmental distribution of 1,2,3 trichlorobenzene (TCB). Nearly 80% partitions into the atmosphere with 18% in soil.

The Level II calculation simulates a situation in which chemical is continuously discharged into the multimedia environment (typically at a rate of 1000 kg/h) and achieves a steady-state and equilibrium condition at which input and output rates are equal. The task is to deduce the rates of loss by reaction in all media and advection in air and water and by sediment burial. From experimental reaction rate data for each chemical, a first order rate constant or half-life is selected for each medium. Often these rates are in considerable doubt.

Table 2 gives an example for TCB indicating that this chemical tends to be removed mainly by advection in air (88%) but with 11% removal by reaction in air. It will persist for approximately 110 hours or 4.5 days.

The third Level III calculation avoids the assumption of inter-media equilibrium, which is recognized as being excessively simplistic and even misleading. In the interests of algebraic

Table 1
Environmental media dimensions, Z values and Level I
distribution of 100 tonnes of 1,2,3 trichlorobenzene
(TCB) at 25°C

Phase	Air	Water	Soil	Sediment	Susp. Sed.	Fish
volume (m^3)	10^{14}	$2x10^{11}$	$9x10^{9}$	10^{8}	10^{6}	$2x10^{5}$
depth (m)	1000	20	0.1	0.01	-	-
area (m^2)	$100x10^{9}$	$10x10^{9}$	$90x10^{9}$	$10x10^{9}$	-	-
fugacity capacity (Z) ($mol/m^3.Pa$)	$4.03x10^{-4}$	$4.13x10^{-3}$	1.02	2.05	6.46	2.60
concentration (mol/m^3)	$7.97x10^{-7}$	$8.17x10^{-6}$	$2.02x10^{-3}$	$4.05x10^{-3}$	0.0128	$5.14x10^{-3}$
amount (%)	79.73	1.63	18.22	0.4	0.01	0.001

fugacity = 1.09×10^{-5} Pa

Table 2
Level II distribution and removal rates of 1,2,3 trichlorobenzene
(TCB) for a continuous discharge of 1000 kg/h

	Air	Water	Soil	Sediment	Susp. Sed.	Fish
Adv. flow (m^3/h)	10^{12}	$2x10^{8}$	-	2000	-	-
Adv. residence time (hours)	100	1000	-	$5x10^{4}$	-	-
React. half life (hours)	550	1700	5500	$1.7x10^{4}$	-	-
Conc'n (mol/m^3)	$4.87x10^{-9}$	$4.98x10^{-8}$	$1.24x10^{-5}$	$2.47x10^{-5}$	$7.73x10^{-5}$	$3.14x10^{-5}$
Amount (%)	79.73	1.63	18.22	0.41	0.01	0.001
Reaction (%)	11.13	0.07	0.25	0.02	-	-
Advection (%)	88.38	0.18	-	0.001	-	-

fugacity = 1.21×10^{-5} Pa
residence times (hours) overall 111 by reaction 987 by advection 125

simplicity only the four primary media are treated for this level. The task is to develop expressions for intermedia transport rates of the various diffusive and non-diffusive processes as described by Mackay (1991). This is done by selecting values for 12 intermedia transport velocity parameters which have dimensions of velocity (m/h or m/year), and are applied to all chemicals. These velocities are used to calculate seven intermedia transport parameters which depend on the environmental conditions and the chemical.

It is desirable to calculate new "bulk phase" properties for the four primary media which include the contribution of dispersed phases within each medium as described by Mackay and Paterson (1991). The air is now treated as an air-aerosol mixture, water as water plus suspended particles and fish, soil as solids, air and water, and sediment as solids and pore-water. The necessity for introducing this complication arises from the fact that much of the intermedia transport of the chemicals occurs in association with the movement of, or in, these dispersed phases.

Four steady state mass balance equations can be written, one for each medium, resulting in a total of four unknown fugacities, enabling simple aglebraic solution. From the four fugacities, the concentration, amounts and rate of all transport and transformation processes can be deduced, yielding a complete mass balance.

The new information from the Level III calculation is the effect of intermedia transport on chemical fate, i.e. the extent to which chemical discharged into one medium tends to migrate into another. This migration pattern depends strongly on the proportions of the chemical discharged into each medium, indeed the relative amounts in each medium are largely a reflection of the locations of discharge. It is difficult to interpret these mass balance diagrams because, for example, chemical depositing from air to water may have been discharged to air, or to soil from which it evaporated, or even to water from which it is cycling between water and air.

To simplify this interpretation, we find that it is best to conduct three separate Level III calculations in which unit amounts (1000 kg/h) are introduced individually into air, soil and water and a fourth with discharges into all media in appropriate amounts. Direct discharges to sediment are unlikely and are not considered here. If, for example, the intermedia transport rate is small compared to the reaction and advection values, the discharged chemical will tend to remain in the discharge or "source" medium with only a small proportion migrating to other media. Conversely, if intermedia transport is rapid, the chemical is likely to become widely distributed. This behaviour is observed for persistent substances such as PCBs which have very low rates of reaction.

Table 3 gives an illustration of this calculation for TCB.

Table 3
Level III distribution of 1,2,3 trichlorobenzene
for four emission scenarios.

Emissions (kg/h)			Concentration (mol/m^3)				Amount (kg)				Total amount (kg)
Air	Water	Soil	Air	Water	Soil	Sediment	Air	Water	Soil	Sediment	
1000	0	0	4.9×10^{-6}	3.1×10^{-6}	2.5×10^{-6}	5.3×10^{-6}	4.9×10^{5}	6.2×10^{3}	4.5×10^{4}	2.7×10^{3}	5.4×10^{5}
0	1000	0	3.0×10^{-6}	7.5×10^{-6}	1.5×10^{-6}	1.3×10^{-3}	5.4×10^{4}	2.7×10^{5}	5.0×10^{3}	1.2×10^{5}	4.5×10^{5}
0	0	1000	1.9×10^{-6}	8.8×10^{-6}	1.5×10^{-5}	1.5×10^{-6}	3.4×10^{4}	3.2×10^{3}	4.8×10^{6}	1.4×10^{5}	4.8×10^{6}
600	300	100	4.0×10^{-6}	2.3×10^{-6}	1.5×10^{-4}	3.9×10^{-4}	7.3×10^{4}	6.3×10^{4}	4.9×10^{6}	3.6×10^{4}	6.6×10^{6}

Table 4
Illustrative calculation of media concentrations
and human exposure routes of TCB.

Exposure Route	Media conc'n (g/m^3)	Intake rate m^3/day	Actual intake (µg/day)
air inhalation, water and food ingestion	7.3×10^{-7}	20	14.6
water	4.13×10^{-4}	0.002	0.83
fish	5.7×10^{-3}	2.5×10^{-4}	1.4
root vegetation	0.032	1.5×10^{-4}	4.8
folier vegetation	0.0047	3.0×10^{-4}	1.4
dairy	7.5×10^{-6}	2.5×10^{-4}	0.002
meat	0.0047	5.0×10^{-6}	0.23
total			23.3

A notable feature of this assessment is that chemicals do not have a single behaviour profile, their behaviour, concentrations and hence exposure are profoundly affected by how they enter the environment. 1 kg of chemical discharged to air, water or soil result in very different sets of concentrations and thus human exposures. Perhaps discharges to different media should be regulated quite differently.

The final product of the Level III calculation is thus a series of concentrations (arising from discharges to air, water and soil) in the bulk media, and in the components of these media such as fish and soil solids.

Exposure Media Concentrations

The next step is to deduce concentrations in human exposure media. Concentrations in air, water and soil (which may be inadvertently ingested) are readily calculated. Fish concentrations are deduced using a bioconcentration factor. A major task, which has been the focus of much of our attention, is the estimation of concentrations in vegetation (e.g. Paterson and Mackay 1989, 1991 and Paterson et. al. 1991). Briefly, we believe that it is reasonable to assume that root vegetables achieve equilibrium with soil, and foliar vegetation with air. The remaining problem is to assign fugacity capacities to various plant tissues. Expressions have been developed to calculate these values (Paterson and Mackay, 1991).

More difficult is the calculation of concentrations in domestic animals and dairy products, although progress is being made in estimating bio-transfer factors along these food chains.

The final result is a series of concentrations in these exposure media in units such as g/m^3.

Exposure

From published information on rates of inhalation, water and food consumption for groups of individuals it is possible to suggest rates of exposure to the various media in units such as m^3/day. For example, for air 20 m^3/day may be appropriate, with 0.002 m^3/day applying to water.

The last step is simply to estimate exposure as the product of media concentrations and consumption rates, i.e.

$$g/day = g/m^3 \times m^3/day$$

The total exposure can be estimated and the dominant exposure routes determined. Table 4 illustrates this calculation for TCB. For this multimedia chemical, approximately 63% of total exposure is due to air inhalation, with 6% due to consumption of fruit and vegetables and 1% each due to ingestion of fish and water.

Management and Regulation

From the regulatory viewpoint, these results can be used in several ways.

It is possible to compare media concentrations with objectives or guidelines, for example Provincial air or water quality objectives.

An interesting aspect of objectives-setting emerges from this analysis. The model predicts the fugacities in the various media. Often, these fugacities are fairly similar, i.e. they often lie within an order of magnitude of each other although air fugacities tend to be lower as a result of rapid advection. This is especially the case for persistent chemicals which survive long enough in the environment to approach thermodynamic equilibrium. If this behaviour is accepted, it can be argued that multimedia objectives should take into account this tendency, i.e. the objectives should be concentrations which are fairly close to equilibrium. It is pointless to have an objective for water which corresponds to an intolerable air concentration, because water near the objective can only occur in association with air in close contact with it which exceeds the air objective. Likewise fish concentrations should relate to the corresponding equilibrium water and sediment concentrations.

It is important to discriminate between development of objectives using this multimedia equilibrium assessment of exposure with mere consideration of all exposure media independently.

An outcome of this argument is that a very simple approach to multimedia standard setting is to decree a single objective fugacity applicable to all media. Selection would be on the basis of the most strictly controlled medium from an exposure viewpoint. Work is currently underway to explore this issue in more detail.

The second application is that the total dosage can be compared with tolerable daily intakes and the primary routes of exposure determined.

Third the results can be used to suggest environmental and food basket monitoring strategies for chemicals by indicating the likely magnitudes of concentrations which will result from specified discharge rates. Often, the model calculations show that these concentrations will be well below detection levels, so analysis is doomed to yield "non detects."

Fourth, for new chemicals the only feasible method of assessing likely exposure, and thus tolerable discharge rates, is by some form of modelling approach as described here.

Finally, it is now increasingly accepted that some chemicals should be "sunsetted." This is likely to become a contentious process when chemicals in profitable commerce are subjected to scrutiny as candidates. The selection process should thus be based on a foundation of sound science, with chemicals being assessed rationally and openly for relative hazard. Models of the type described here can play a role in this process.

Conclusions

A generic modelling approach has been described in which chemicals are subjected to increasingly rigorous calculation of environmental behaviour with subsequent estimation of concentrations in exposure media and of exposure or dosage. It is believed that the approach can be readily adapted to specific regions such as parts of Ontario and can contribute to more effective multimedia environmental management of chemicals.

It is a pleasure to acknowledge the Ministry of Environment's Hazardous Contaminants Coordination Branch who have supported this work during the last few years.

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FOOD WEB DYNAMICS AND CONTAMINANT EXPOSURE IN AQUATIC ECOSYSTEMS

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ABSTRACT

Organochlorine concentrations were determined for 30 relatively common species of the Lake St. Clair food web in order to quantify the importance of biomagnification in regulating chemical exposure dynamics in aquatic ecosystems. Specifically, organism / water fugacity ratios were developed for octachlorostyrene using total water concentrations (0.1 ng/L) and bioavailable water concentrations (0.03 ng/L). Theoretically, all aquatic organisms should be near chemical equilibrium with the water phase if water is the primary uptake route (bioconcentration): and at equilibrium, the animal / water fugacity ratio should be 1. Measured values of the fugacity ratio for octachlorostyrene in Lake St. Clair were as high as 14 when calculated as a function of total water concentrations, and as high as 450 for bioavailable water concentrations. Fugacity ratios in Lake St. Clair are species specific, and are related to both the trophic position and the feeding strategy of the species.

INTRODUCTION

There remains considerable debate as to the relative importance of biomagnification (the uptake of chemical from food) in aquatic ecosystems. For example, Macek et al. (1979) considered biomagnification to be relatively unimportant in determining the distributions and levels of organic contaminants in aquatic food webs, whereas Borgmann and Whittle (1983) and Thomann and Connolly (1986) concluded biomagnification was an important process in Lakes Ontario and Michigan respectively. Although it is accepted that chemical uptake from water and food (bioaccumulation) can result in an array of toxicological responses, the critical route of exposure remains to be resolved for many chemicals.

It is important to resolve the role of biomagnification in regulating contaminant exposure dynamics in order to set water quality objectives and determine appropriate consumption advisories. The current inability to quantify exposure dynamics for the many chemical of concern has resulted in much confusion as to the establishment of cause - effect linkages in the field. Current strategies for setting environmental guidelines assume that thermodynamic models give a close approximation to chemical uptake and release (exposure), and consider biomagnification to be a relatively unimportant process in regulating chemical dynamics in aquatic ecosystems.

Originally, water was considered to be the most important route of chemical uptake. Support for this argument was provided by the close relationship of the bioconcentration factor (BCF) and the n - octanol water partition coefficient (Kow). Essentially, the BCF was found to be related to Kow such that;

$$Kow = Lf * BCF \qquad (1)$$

where Lf is the lipid content of the organism. Biological processes such as predator - prey relationships had no or little influence on regulating organochlorine concentrations in aquatic organisms.

This thermodynamic approach is supported by the fact that the uptake and elimination of organic chemicals are passive processes. Thus it is impossible for contaminants to move against the chemical gradient. The thermodynamic model predicts that all organisms will have similar contaminant concentrations per unit lipid. It is possible to test the thermodynamic model by determining if organisms from different trophic levels and with different feeding strategies (pelagic versus benthic) are in or approaching chemical equilibrium with the water phase.

The aim of this study was to quantify contaminant distributions in the Lake St. Clair food web. By assessing chemical concentrations based on lipid content, it was possible to test the prediction that there would be no significant difference in contaminant concentrations among trophic levels or between species belonging to benthic or pelagic food chains. Specifically, we measured chemical distributions using animal - water fugacity ratios (fa / fw) as developed by Connolly and Pederson (1988).

METHODS AND THEORY

The fugacity of a chemical (f) is measured as a function of the chemical concentration in a given phase (C) divided by the fugacity capacity of the phase (Z), ie;

$$f = C/Z \qquad (\ 2\ )$$

The fugacity capacity of water (Zw) is inversely proportional to its Henry's Law constant such that

$$Zw = 1/H \qquad (\ 3\ )$$

and the fugacity of a chemical in water is therefore quantified as

$$fw = Cw * H \qquad (\ 4\ )$$

To determine the fugacity of a chemical in an organism (fa), it is necessary to determine the fugacity capacity of organisms (Za), which is related to the lipid content of a particular organism. Assuming that n-octanol is a surrogate of the general lipid content of organisms, it is possible to relate the fugacity capacity of an organism to the octanol water partition coefficient of a chemical. The octanol water partition coefficient (Kow), is determined as the ratio of the fugacity capacity of a chemical in octanol divided by the fugacity capacity of the chemical in water

$$Kow = Zo \ / \ Zw \qquad (\ 5\ )$$

If octanol is accepted as a good surrogate of lipid , then

$$Kow = Za \ / \ Zw \quad \text{or}$$

$$Za = Kow * Zw = Kow \ / \ H \qquad (\ 6\ )$$

and the fugacity of a chemical in an organism is

$$fa = Ca * H \ / \ Kow. \qquad (\ 7\ )$$

Therefore the fugacity ratio fa/fw can be directly determined as

$$fa/fw = Ca \ / \ Cw * 1 \ / \ Kow. \qquad (\ 8\ )$$

Theoretically, if chemical uptake and elimination are primarily associated with the water phase, all organisms should reach or tend to a chemical equilibrium with the water phase such $fa/fw = 1.0$. Values above 1 would not only indicate that biomagnification was occurring but would also indicate the relative importance of biomagnification. Values less than 10 would generally be insignificant with respect to the magnitude of the BCF for hydrophobic organochlorines which can range from 100,000 to over 10,000,000. Values over 100 would suggest important differences in exposure are occurring among species in the food web.

A variety of species from among and within different trophic levels were sampled in the Lake St. Clair ecosystem during 1988 to 1991 in order to determine if fugacity ratios were species dependent, and to determine if the measured ratios were related to trophic level and/or feeding strategies. Octachlorostyrene (OCS) was selected as the test chemical because of its high hydrophobicity, and because the major source of OCS in the Great Lakes is just upstream of the Lake St. Clair ecosystem.

Total chemical concentrations in the water phase were determined by extracting 4 L of water with hexane. Bioavailable chemical concentrations were determined by deploying the freshwater clam (Elliptio complanata) which had previously been calibrated by Russell and Gobas (1989). After 21 day exposures, bioavailable water concentrations were determined as

$$Cw = Cm / (k1/k2) (1 - \exp -k2t) \qquad (9)$$

Deployment sites were at the mouth and headwater of the St. Clair and Detroit Rivers respectively.

Chemical analysis was performed by gas chromatography as described by Hebert and Haffner (1991). All data were adjusted to express contaminant concentrations on a per unit lipid basis.

RESULTS

Fugacity ratios of octachlorostyrene for species of the pelagic and benthic food webs based on total water concentrations (0.10 ng/L) were small (<14). Although there is some evidence for biomagnification, it would appear the process is not important in regulating contaminant concentrations in aquatic species when compared with bioconcentration. Differences in interspecific exposure dynamics were considered to be relatively small.

It has been noted, however, that total water concentrations do not reflect the bioavailable compartment of truely dissolved chemical. As this is the compartment being tracked by biological systems, it would be appropriate to quantify the fugacity ratio with respect to this chemical form.

Figure 1 illustrates fugacity ratios based on bioavailable chemical concentrations for 30 species of the Lake St. Clair food web. Fugacity ratios ranged as high as 450, and there are strong interspecific differences. Plankton (primarily zooplankton) levels averaged 4, whereas ratios for forage fish species ranged between 2 and 20, the lowest ratio was associated with brook silversides (*Labidesthes sicculus*) which are obligate surface feeders and the highest with the benthic feeding bluntnose minnow (*Pimephales notatus*) and with alewifes (*Alosa pseudoharengus*) (Figure 1 a).

Benthic invertebrate species had fugacity ratios similar to that observed in the pelagic food web (2 to 16) (Figure 1 b). This is not unexpected in a shallow, productive lake where most of the benthic organisms will be feeding on the rain of planktonic material falling out of the water column.

Much higher ratios (fa/fw > 50) were observed for larger benthic vertebrate species such as carp and channel catfish (*Cyprinus carpio*, *Ictalurus punctatus*), and for true piscivores like walleye and smallmouth bass (*Stizostedion vitreum*, *Micropterus dolomieui*) where fa/fw > 70 was commonly observed. Ratios over 100 were observed for benthic invertebrates such as stonecats , redhorse and the predatory northern pike (*Noturus flavus*, *Moxostoma erythrurum*, and *Esox lucius* respectively).

DISCUSSION

Animal / water fugacity ratios for organisms in the St.Clair ecosystem strongly support the hypothesis that food web dynamics can play an important role in determining contaminant exposures. The consistency with which larger benthic vertebrates exhibit high ratios, (also observed within the forage fish trophic level), suggests that species comprising the benthic food web are exposed to higher concentrations of chemicals than species occupying equivalent trophic levels of the pelagic food chain. The high levels observed in pisciovores such as pike and smallmouth bass can be a function of both intenive trophic interactions (such as cannibalism) and strong benthic - pelagic couplings. In the food web of Lake St. Clair, benthic - pelagic coupling occurs primarily at the trophic level of the forage fish. In deeper lakes , this coupling might be at a lower trophic level based on the relative abundance of invertebrates such as *Mysis*, *Gammarus* and *Diporeia*. These species effectively create another trophic interaction between the sediments and the pelagic sport fish, and result in further potential to augment the importance of the biomagnification process. Essentially, the fugacity ratios observed in Lake St. Clair might well be minimal, based on the dominating effect of the plankton on benthic levels, the lack of microbial loops to process the sedimenting particulates and the coupling of benthic - pelagic food chains occurring only at a higher trophic level.

The interspecific differences in the fugacity ratio reported in this study are temporally stable, in that the pattern is consistently shown by data collected annually over a three year period. This pattern is important in both the setting of both water quality guidelines and for setting consumption advisories. Only be describing and quantifying the exposure dynamics of chemical will cause - effect linkages be developed. As quantified in this study, exosures are higher in benthic food webs as a result of biomagnification. These higher exposures might well be a major factor in the prevalence of toxicological stress indicators observed in the benthic food web.

AKNOWLEDGMENTS

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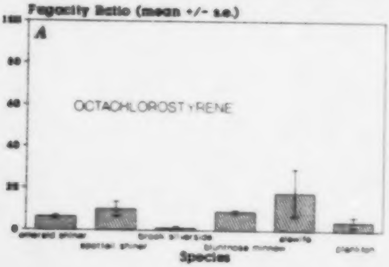
FICURE ONE

Fugucity ratios (fa/fw) for 30 species of the Lake St. Clair food web. (Mean + s.e.). Figure 1a summarizes the ratio for the pelagic food web, and Figure 1b summarizes the ratio for the inverebrate benthic food web. Figures 1c, 1d and 1e illustrate fugacity ratios for benthic vertebrates and piscivores of the Lake St. Clair food web.

Lake St. Clair Food Web



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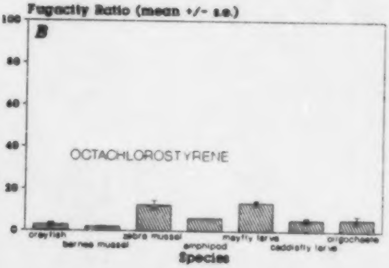

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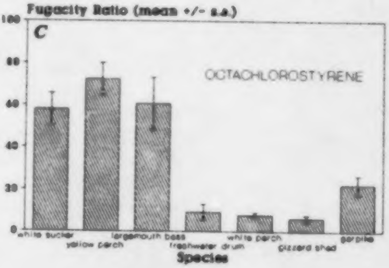

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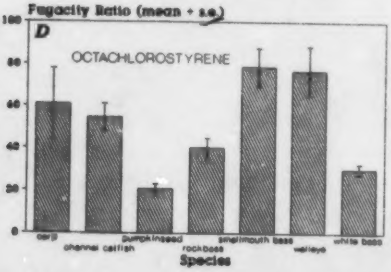
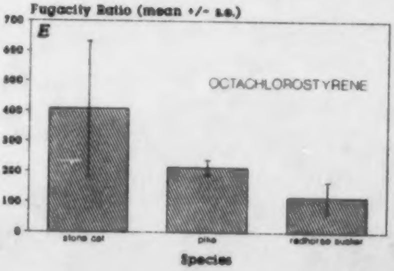


Lake St. Clair Food Web



A16

PCB DYNAMICS IN A SOUTHWESTERN ONTARIO CREEK

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INTRODUCTION

Polychlorinated bipyhenyls (PCBs) are a group of ubiquitous, man- made chemicals that, through atmospheric deposition (Eisenreich et. al., 1981; Patton et al., 1989), have spread throughout aquatic environments resulting in contamination of biota, sediments and vegetation. In the early 1980's, monitoring of Pottersburg Creek, London, Ontario revealed that much of the creek sediments were contaminated with PCBs resembling mixtures of Aroclor 1248, 1254, and 1260. Remediation efforts between 1985 and 1986 included the removal of sediments from the most contaminated areas of the creek, however, in the fall of 1987 subsequent monitoring of the remediated areas revealed that the sediments had become recontaminated. The discovery of PCBs in Pottersburg Creek has provided an opportunity to gain a better understanding of their movement in aquatic ecosystems and the mechanism of PCB transfer to higher trophic levels. Because the three Aroclors found in Pottersburg Creek have a log K_{ow} of between 5.8 and 7.5, the direction of this study was towards the synthesis of a food web in order to explain contaminant levels in biota. If the biota show an increase in PCB body burden with increasing trophic status beyond that which can be explained by variation in lipid content, then one could conclude that PCBs biomagnify through aquatic food webs resulting in highest accumulations in top predators. In addition to the above, the ultimate objective of this project is to develop a model in order to predict the time required for PCB levels in aquatic biota to reach the IJC (1975) aquatic life protection guideline of 100 ng/g.

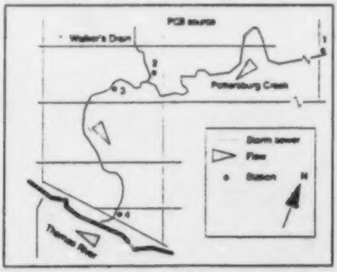

Figure 1. Location of monitoring stations along Pottersburg Creek.

MATERIALS AND METHODS

Collection and analyses of stream components, 1988 - 1991.

Samples of water, sediment, algae, aquatic macrophytes, various macroinvertebrates and fish were collected for biomass and PCB analysis at 4 sites along Pottersburg Creek (Fig.1). Station 1 was used as a reference site and Stations 2, 3 and 4 were located consecutively downstream of the point source of PCBs.

Invertebrates gathered for biomass and density determination were collected with a T-sampler enclosing an area of 0.05m^2, and sieved through a 300 μm bag. Invertebrates were sorted live from the debris in white enamel trays and subsequently preserved in 70% ethanol for later identification and enumeration. All organisms were identified to the lowest taxonomic level, usually genus, except for oligochaetes which were identified to species.

Invertebrates gathered for PCB analysis were collected and sorted live in white enamel trays until an adequate weight was obtained for analysis (i.e. 3g or more). Animals were separated into their respective classes (e.g. oligochaetes, chironomids, leeches) and weighed to the nearest 0.01g. Samples were subsequently wrapped in hexane-rinsed aluminum foil, placed in plastic Whirl-Pak bags and kept frozen until analyzed. The samples were analyzed for total PCBs and lipid with results being reported on a wet-weight basis. Analyses were carried out at the Ontario Ministry of the Environment's laboratory in Rexdale using packed column gas chromatography (OMOE, 1986).

Construction of a Food Web

Fish were collected with a seine net from Stations 1,2,3 and 4 and preserved in 20% formalin. Collections were made in the summer and winter of 1988 and the summer of 1989. Fish stomachs were dissected and a list of food items was compiled. A food web of Pottersburg Creek was synthesized from feeding observations and gut contents analysis. Points of PCB entry and loses were also identified.

Determination of PCB uptake and depuration rates

Uptake experiments were set up for the following biota: crayfish, leeches, fish, and oligochaetes. Crayfish (*Orconectes* sp.) were captured in the fall of 1990 from the Eramosa River, Guelph, Ontario. A total of 36 crayfish were placed in 6 cylindrical wire cages which were 45 cm long and had a diameter of 20cm. Leeches (*Nephelopsis obscura*) were purchased from a local bait dealer. Approximately 36 leeches were placed in each of 3 wooden cages measuring 45cm X 30cm X 20cm. Two opposite sides of each cage had 6cm X 18cm holes which were covered with a 300 μm mesh screen to facilitate water flow. The tops of two of the cages were covered with 300 μm mesh screen while the other cage was covered with a 2mm mesh fibreglass screen. The first cage contained contaminated sediments collected from Station 2. The second cage contained contaminated sediments from station 2 which had been previously frozen to kill any indigenous organisms and the third cage contained only clean rocks. Oligochaetes (*Lumbriculus variegatus*) were purchased from a local pet store and approximately 100 grams of worms were

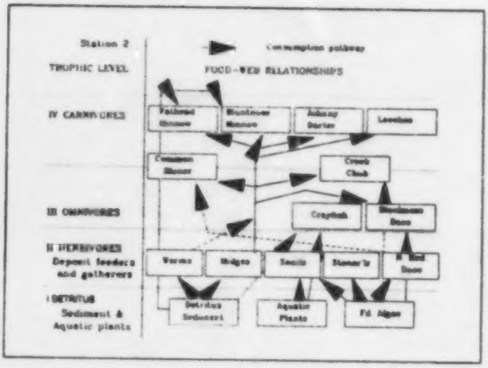
Station 2
Consumption pathway
TROPHIC LEVEL
FOOD-WEB RELATIONSHIPS
IV CARNIVORES
Fathead Minnow
Bluntnose Minnow
Johnny Darter
Leeches
Common Shiner
Creek Chub
III OMNIVORES
Crayfish
Blacknose Dace
II HERBIVORES
Deposit feeders and gatherers
Worms
Midges
Snails
Stonefly
Dace
I DETRITUS
Sediment & Aquatic plants
Detritus Sediment
Aquatic Plants
Fil Algae

Figure 2. Food web of Station 2 outlining major predator - prey relationships.

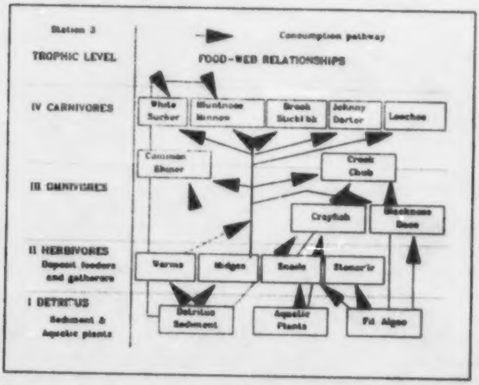
Station 3
Consumption pathway
TROPHIC LEVEL
FOOD-WEB RELATIONSHIPS
IV CARNIVORES
White Sucker
Bluntnose Minnow
Brook Stickleback
Johnny Darter
Leeches
Common Shiner
Creek Chub
III OMNIVORES
Crayfish
Blacknose Dace
II HERBIVORES
Deposit feeders and gatherers
Worms
Midges
Snails
Stonefly
I DETRITUS
Sediment & Aquatic plants
Detritus Sediment
Aquatic Plants
Fil Algae

Figure 3. Food web of Station 3 outlining major predator - prey relationships.

placed in each of 2 wooden cages which had the same dimensions as those described above for leeches. The top of each cage was covered with a 300 μm mesh screen while the sides were covered with 100 μm mesh screens. The first cage contained contaminated sediment collected from Station 2 which had been previously frozen and the second cage contained only clean rocks. Fish (*Pimephales promelas*) were collected from Dorsett Ontario and approximately 400 fish were placed in a wire circular cage which was approximately 2m in diameter and whose mesh size was 0.63 cm. The bottom of the cage was left open so the fish were exposed to creek sediments, vegetation and food.

The cages containing the biota were anchored to the stream bed with rocks at the contaminated site (Station 2) and subsequently collected after the following days: day 8, 15, 23, 36, 50, 58, 71 for crayfish; day 8, 11, 16, 29, 51, 85 for leeches; day 7, 10, 16, 29, 43, 56 for worms; day 10, 12, 20, 35 for fish.

Depuration experiments were conducted for fish, crayfish and worms. Fish and crayfish were collected from contaminated areas of the creek (Station 2 and 3 respectively) and placed in 45 L aquaria. The water was changed every 4 days to prevent PCB accumulation. Worms were collected from Station 2 and placed in 45 L aquaria which contained silica sand. Fish and crayfish were collected after 4, 6, 10, 18, 34, and 66 days and worms after 2, 5, 11, 23, 35 and 63 days. Each group of animals was weighed live to the nearest 0.01g, wrapped in hexane-rinsed aluminum foil, placed in Whirl-Pak plastic bags, and frozen until analyzed. Replicate samples were submitted for each time period where possible. In addition, samples of all groups of animals were submitted for PCB analysis prior to the start of the depuration experiments.

RESULTS AND DISCUSSION

Food web relationships

The food webs of Station 2 and 3 (Fig. 2 and 3) were found to be similair in species composition, however, quantitatively they differed with respect to biomass. Crayfish and chironomids dominated Station 3 while worms were the dominant invertebrates found at Station 2. Sediment at Station 2 is typically a fine silt which is 15 - 30 cm deep at places. In the summer months, *Cladophora* is dominant throughout this area with some *Potamageton* growing along the edges of the creek. These overgrowths of algae die off in the late fall and are subsequently carried downstream. Station 3 is characterized by a shallow layer of sand and gravel overlaying hard compact clay. *Cladophora* and *Potamageton* are present but in lesser quantities. Station 4 had a greater diversity of habitat than Station 2 and 3: sediments consisted of large rocks, gravel and sand overlaying compact clay. Large riffles, pools and under-cut banks are present.

PCB concentrations in sediments from Station 2, 3 and 4 decreased temporally as well as spatially from 1988 to 1990. In 1988, Station 2 sediments contained 4130 ng/g (dry weight)

PCB while 1990 sediments contained 885 ng/g. PCB concentrations at Station 3 have decreased from 920 ng/g to 63 ng/g while concentrations at Station 4 have dropped from 60 ng/g to 30 ng/g. Presently, PCB concentrations in sediments remain above 500ng/g at Station 2 while concentrations at the other 2 stations are much lower, i.e. less than 100 ng/g, for most of the year.

Even though the initial source of PCBs into Pottersburg Creek has been alleviated, the sediments remain a continuing source to biota and vegetation. PCBs bound to sediments may be redistributed to the water by scouring caused by catastrophic drift, bioturbation and desorption processes thus making them more available to biota and aquatic plants (Klump et al. 1987; Karickhoff and Morris 1985). In 1990, PCB concentrations in water were below detection limits (<20 ng/L) for most of the year, except after heavy rainfall events when concentrations reached 330 ng/L at Station 2.

The uptake of chlorinated hydrocarbons by phytoplankton (Biggs et al. 1980; Sodergren and Gelin 1983) aquatic macrophytes (Strek and Weber 1982) and filamentous algae, e.g. *Cladophora*, (Mowrer et al. 1982; Larsson 1987) is rapid and initially follows first order kinetics (Larsson 1987). Thus, the partitioning process governs PCB uptake and in turn is dependent on the concentrations of PCBs in the water (Larsson 1987). In 1988, algae and aquatic macrophytes collected at Station 2 accumulated substantial quantities of PCBs, 150 ng/g and 770 ng/g, respectively. In 1990, PCB concentrations in *Cladophora* declined to 76 ng/g while PCB concentrations in *Potamogeton* were non-detectable. No PCBs were detected in algae and aquatic macrophytes at Station 3. Filamentous algae (*Cladophora*) and aquatic macrophytes (*Potamogeton*) are consumed by scrapers, i.e. snails and shredders,i.e. crayfish. Algae are also consumed by a variety of fish in Pottersburg Creek. Analysis of gut contents has revealed that filamentous algae are the primary diet of the northern redbelly dace (*Chrosomus eos*) and the stoneroller (*Campostoma anomalum*). Common shiners (*Notropis cornutus*) and blacknose dace (*Rhinichthys atratulus*) also consume filamentous algae but to a lesser extent. As no metabolism or elimination of PCBs has been recorded in algae (Hutzinger et al. 1974), the rapid adsorption and uptake of PCBs by algae and aquatic macrophytes constitute a means for the introduction of these compounds into food webs (Mahanty 1986).

Algae and aquatic macrophytes are a food source for snails and crayfish. In addition, crayfish eat detritus, and other organisms (Hynes 1970), which in turn are known to accumulate or sorb PCBs. In 1988, *Helisoma sp.* collected from Station 3 had PCB residues of 360 ng/g and young of the year crayfish from Stations 2, 3 and 4 had residues of 960 ng/g, 720 ng/g and 320 ng/g, respectively. Decreasing body burdens in crayfish indicate a reduction of PCB availability with increasing distance from Walkers Drain (Stn. 2). Older crayfish from Station 3 were noted to accumulate 40% more PCBs than young of the year. This would suggest that length of exposure, coupled with higher lipid levels in the older individuals, may have an effect on PCB bioaccumulation. In 1989 and 1990, snails collected at Station 3 showed no accumulation of PCBs, however, snails collected from Station 2 in 1990 showed accumulations of 280 ng/g. PCB residues in crayfish collected from Station 2, 3 and 4 varied depending on the size of the animal as well as the lipid content albeit, concentrations were noted to be lower than in the previous year.

Crayfish and snails are eaten by a variety of fish (Scott & Crossman 1972). Gut contents analysis confirmed the ingestion of snails by creek chub (*Semotilus atromaculatus*) in Pottersburg Creek (Station 3), however no crayfish were found in the stomachs of the fish. Therefore, snails may contribute to the overall PCB body burden of fish such as creek chub.

The sediments remain a continuing source of PCBs to chironomids and worms. Ingestion of sediment (Roberts and Meier 1982) and PCB contaminated organic particles after they settle on the sediment (Oliver 1984) is one route of contamination. In addition, tubificid worms have been shown to feed selectively on sediments high in organic matter (Brinkhurst et al., 1972). As PCBs are believed to be sorbed to the organic fracton of sediments, worms may be selectively ingesting PCBs. Meier and Rediske (1984) have been able to show that larvae of the midge *Glyptotendipes barbipes* can accumulate significant concentrations of PCBs from substrate feeding alone. Initial bioaccumulation by midges has been shown to be very rapid with steady state concentrations being reached in 4 to 5 days (Swindoll & Applehans 1987). While uptake is very rapid, PCBs have been shown to be poorly eliminated from benthic organisms (Swindoll & Applehans 1987; Meier & Rediske 1984). Thus, chironomids and worms serve as major vectors for the transfer of PCBS to higher trophic levels.

PCB residues in oligochaetes and chironomids were among the highest for 1988 biota, reaching concentrations of 3030 ng/g and 1890 ng/g respectively in the summer months. Residues in 1990 decreased to less than 1000 ng/g for worms and less than 500 ng/g for chironomids.

Gut contents analysis of fish and feeding observations revealed that chironomids and worms are major food items of all fish species except the northern redbelly dace and the stoneroller who feed primarily on algae. These findings are in agreement with Gilliam et al., (1989) who showed that fish such as creek chub consume worms. In addition, leeches are also predators of chironomids and worms. Leeches (*Erpobdella punctata*) captured from Pottersburg Creek were observed eating chironomids in captivity. As well, several authors have documented that the main food items of leeches are oligochaetes and chironomids (Davies et al 1981; Anholt 1986). The decrease of PCBs in leeches mirrors the decrease in their prey whereas sediment concentrations have remained constant for these areas of the creek.

Leeches were found to occupy the same trophic level as fish consequently PCB concentrations in leeches approached and at times exceeded those concentrations found in fish. In the summer of 1988, PCB residues in leeches were 2000 ng/g at Station 2 and 1060 ng/g at Station 3. In 1989, residues dropped to 1100 ng/g at Station 2 and 700 ng/g at Station 3. Leeches are preyed upon by a variety of fish (Scott & Crossman 1973) but were not found to be major food items of the fish found at Station 2 and 3 in Pottersburg Creek.

The ten species of fish that have been identified from Pottersburg Creek can be grouped into four categories based on their primary diet: algae grazers [stoneroller (*Campostoma anomalum*), northern redbelly dace (*Chrosomus eos*)]; chironomid feeders [brook stickleback (*Culaea inconstans*), johnny darter (*Etheostoma nigrum*)]; bottom ooze feeders [white suker (*Catostomus commersoni*), bluntnose minnow (*Pimephales notatus*), fathead minnow (*Pimephales promelas*)]; and general feeders [common shiner (*Notropis cornutus*), creek chub (*Semotilus atromaculatus*), blacknose dace (*Rhinichthys atratulus*)]. It is believed that food selection and habitat utilization will have an effect on PCB accumulation in these four groups of fish. PCB concentrations are believed to be the highest in bottom ooze feeders followed by the chironomid feeders, the generalists and finally the algae grazers.

Common shiners collected in July 1988 had lower PCB residues than johnny darters collected from the same stations i.e. (Station 2 shiner - 1960 ng/g, darter - 2780ng/g). The observed differences can be attributed to the position of the fish in the water column as well as their diet. Johnny darters were found to feed primarily on chironomids which themselves exhibited high PCB levels. On the other hand, analysis of common shiner fish stomachs revealed no preferred diet. However, it was noted that in the spring and early summer, their diet consisted primarily of surface insects. Gilbert (1964) found that common shiners usually feed off the surface but will take food off the bottom. In the fall and winter months, the common shiner switches its diet to detritus, sediment, algae or invertebrates depending on their respective availabilities. Thus, depending on the time of year, PCB residues in common shiners may vary depending on their diet.

PCB concentrations in common shiners and johnny darters varied in 1989 depending on station location and lipid content. Moreover, it was noted that PCB concentrations in both species of fish did not decrease over the two year period perhaps as a result of biomagnification. In 1990, PCB concentrations in common shiners collected from most areas of the creek have decreased, however, residues in fish closest to the point source of contamination remain elevated (2100 ng/g). PCB concentrations in the northern redbelly dace, collected from Station 2 in 1990, were as high as 2200 ng/g while concentrations in the blacknose dace ranged between 1400 to 3050 ng/g. PCB concentrations in the stoneroller, collected from Station 3 in 1990, reached 500 ng/g and 580 ng/g in creek chub.

Bioaccumulation of PCBs

The bioconcentration concept suggests that uptake of PCBs is dependant on the log K_{ow} of a chemical and the lipid fraction of an organism. If biota from Pottersburg Creek are indeed uptaking PCBs from the water column then each organism having the same lipid composition and proportion should bioaccumulate the same amounts of PCBs, regardless of their position in the food web (trophic level). The biomagnification concept suggests PCB residues in biota are attributed to the ingestion of contaminated prey which subsequently leads to higher PCB concentrations in predators occupying the top of the food web. Therefore, if uptake of PCBs is through ingestion then biota should accumulate different concentrations of PCBs depending on their position in the food web.

In Pottersburg Creek, PCB concentrations in biota from Station 2 are greater than those at Station 3 and these in turn are greater than concentrations at Station 4 (figure 4), $p = 0.0001$. In addition, the relationship between PCB concentration and lipid was similar between sites, .i.e. the slopes of the lines are equal. Consequently, PCB concentrations in biota are decreasing along the length of the creek away from the point source.

The relationship between PCBs and lipid for biota from Station 2 and 3 (Figure 5) suggests that organisms tend to accumulate PCBs relative to their position in the food web. Fish and leeches occupying the top of the food web, tended to accumulate more PCBs than the lower trophic level organisms. Crayfish in turn accumulated more PCBs than did chironomids at Station 3 and worms at Station 2. Because all data are not yet available, the slope of the lines in Figure 5 were extrapolated from Figure 4 and assumed equal for all biota. As more data becomes available, the actual slopes of the lines will be deduced followed by statistical analysis of the data.

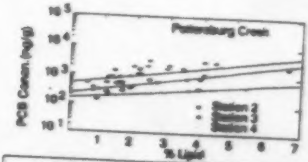

Figure 4. Relationship between PCBs and lipid at different Stations.

Model: PCB = Station * Lipid
R^2=0.57 P=.0001

	DF	F value	P
Station	2	17.74	0.0001
Lipid	1	24.40	0.0001

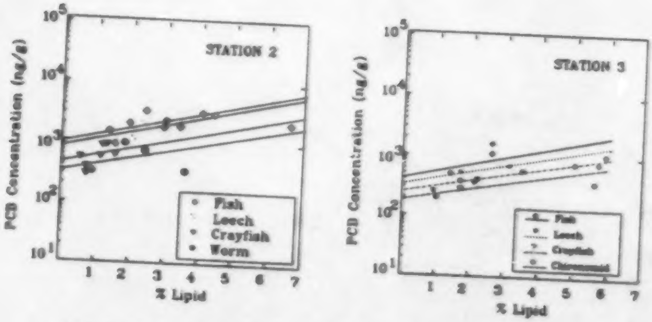

Figure 5. Relationship between PCBs and lipid for biota from different trophic levels at Station 2 and 3.

Uptake and depuration

Uptake and depuration experiments are presently being conducted for fish, crayfish, leeches and worms. Results to date indicate that uptake of PCBs is rapid (Figure 6) however, concentrations were noted to be lower than those from collected biota from the same station (leeches, Stn.2 - 1100 ng/). Lower accumulations are attributed to the short time interval of the experiment, i.e., 85 days. In addition, uptake rates were higher in leeches exposed to creek water, sediments and contaminated food (eg. 500 ng/g lipid in 51 days) compared to leeches only exposed to creek water (eg. 133 ng/g lipid in 51 days) suggesting that the sediments and ingestion of contaminated prey are governing contaminant levels in biota.

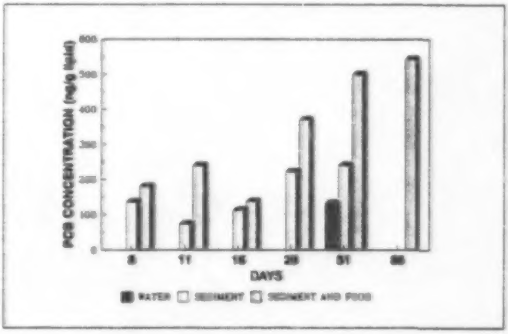

Figure 6. Uptake of PCBs by leeches

CONCLUSION

PCB concentrations in biota, water and sediments from Pottersburg Creek are decreasing with time as well as along the length of the creek away from the point source of PCBs. However, PCB residues in aquatic biota still remain above the IJC aquatic life protection guideline of 100 ng/g with fish showing the highest concentrations.

From within the creek, the sediments remain a continuing source of PCBs to biota. Scouring of bottom sediments caused by catastrophic drift, bioturbation and desorption processes continuously redistribute PCBs making them more available to aquatic biota. Filamentous algae quickly sorb PCBs from the water and in turn are a food source to snails and crayfish. Chironomids and worms ingest contaminated sediment and organic matter after it settles out on the sediment and are a major food source of fish and leeches. This movement of PCBs up the food web consequently results in highest accumulations in leeches and fish as reflected in Figure 5, suggesting that biomagnification may be the mechanism responsible for contaminant levels in biota.

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VOLUME I

SESSION A

ENVIRONMENTAL TRANSPORT AND FATE

POSTER PRESENTATIONS

AP1

THE EFFECTIVENESS OF A STORMWATER MANAGEMENT POND IN THE REMOVAL OF URBAN CONTAMINANTS FROM STORMWATER

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NATURE OF THE PROBLEM

Contaminants in stormwater runoff can seriously pollute receiving water bodies. Stormwater runoff contains such contaminants as, salts, pesticides, coliforms, hydrocarbons, phosphorus, heavy metals, eroded soil and other sediments. Concern relates to recreational water use where high coliform counts can pose a health risk, aesthetic problems with appearance and entrophrication of receiving waters, and damage to fish and other aquatic life from heavy metals and sediment.

In a comprehensive manual on controlling urban runoff in the Greater Washington, D.C. area Schueler (1987) identified wet stormwater ponds as an extremely effective water quality 'best management practice' (BMP). Environment Ontario (1991) reported that although wet ponds are the most common structural BMP used in Ontario, they have limitations - change in hydrologic regime, nutrient and contaminant cycling and release, and other negative impacts on the receiving waters including thermal enhancement and erosion. In the assessment of remedial effectiveness of ponds in Ontario and the Great Lakes Basin, there are additional problems. First, existing wet ponds were designed for quantity control only, exhibit poor performance in quality control and must be retrofitted to improve effectiveness. Second, 'performance' is based on limited data from Washington, D.C., which may not be directly transferable to Ontario climatic conditions. Third, the understanding of pollutant removal processes is very limited. There is a need, therefore, for an interdisciplinary study to identify, through an ecosystem approach, the major processes affecting the mass transfer of critical pollutants including both persistent toxics and nutrients within the urban ecosystem encompassing stormwater ponds, and to assess environmental impacts of stormwater ponds by ecotoxicological methods. The first step is to determine mass balances for water, sediment and key contaminants for a wet ponds under Ontario conditions.

SPECIFIC OBJECTIVES

1) to define the processes involved in the movement of contaminants from urban surfaces

through the soil mantle or over the surface and into wet stormwater management ponds,

2) to incorporate the understanding of these processes into a mass balance model for the pond,

3) to collect three seasons of water quantity and quality data on an event basis for a wet pond in Kingston Township,

4) to describe the effectiveness of the pond in improving stormwater quality for various storm events and under low flow conditions.

ENVIRONMENT ONTARIO'S STAKE IN PROBLEM

Recently, Environment Ontario (1991) reported that

> The most common structural BMP used in Ontario is the water quality pond. Most designs have concentrated on the basic sedimentation capabilities of the devices in attempting to address stormwater quality concerns. Ponds provide many other benefits and can be designed to provide environmental opportunities and enhanced water quality control. They are not however, an all-encompassing solution to stormwater concerns.....Ponds are likely to continue to be an important element in stormwater quality control. Their limitations need to be recognized however, and the special design considerations which often have to be addressed need to be noted. In some cases the problems associated with ponds can be overcome by design. It should be recognized however that ponds are not suited to some applications, especially where baseflow preservation or groundwater recharge are among the concerns driving the BMP plan.

As the capability of an on line stormwater control pond to improve water quality while subject to natural flow variations is not well known, it is necessary to collect and analyze data from existing online detention ponds in an attempt to characterize the hydrologic/water quality processes. Only through this analysis can the value of detention ponds in the control of stormwater quality be determined. Ultimately, the effectiveness of detention ponds must be known for the development of Provincial guidelines for stormwater quality control.

PROGRESS TO DATE

Literature Survey

A comprehensive literature survey has been conducted to define the state-of-the-art regarding the function of stormwater management ponds in the improvement of water quality of receiving waters.

Field Surveys

A field survey program was implemented to determine the characteristics of the creek and the drainage area which includes the Cataraqui Town Centre. The poster display shows the drainage basin, the location and size of directly connected impervious areas, pond plan and cross sections and locations of rainfall gauges and water level control structures and recorders.

Pond Instrumentation

Field work was conducted to install rainfall, water level, flow and water quality monitoring instrumentation. The poster display illustrates the weirs which were designed and constructed by the Department of Civil Engineering for the storm water inlet and the creek inlet to the pond.

Also shown are photographs of the instrumentation system which involves shaft encoders for waterlevel monitoring, a tipping bucket rain gauge and a data logger.

Chemical Constituent Characterization

Field and laboratory studies were conducted to determine natural background levels of major, minor and trace chemical constituents in the runoff and in the pond sediments. The poster display shows results of chemical analyses of water inflow and outflow during selected storm events. Also shown are results of chemical analyses of pond sediments.

Pond Biota Characterization

Field and laboratory studies were conducted to characterize the vegetation and biota in and around the stormwater ponds. Results are summarized on the poster display.

FUTURE DIRECTIONS

At this stage, it is premature to compare findings to earlier work. Anticipated future results include further measurements on water quality and contaminants for runoff events, estimates for the water and chemical balance of the system, and preliminary estimates of the effectiveness of the pond on contaminant removal.

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AP2

BIOCONCENTRATION OF CHLORINATED ORGANIC CHEMICALS IN FIELD EXPOSED FISH.

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Hydrophobic organic chemicals in water have a tendency to accumulate in the lipid tissues of aquatic organisms. The magnitude and rate of chemical uptake has been related to the 1-octanol-water partition coefficient (K_{ow}) of the chemical in question (Russell and Gobas, 1989). However, some chemicals show a bioconcentration tendency orders of magnitude smaller than that predicted from the bioconcentration factor (BCF) K_{ow} linear relationship (Gobas et al.,1989). Organic substances can be completely or partially unavailable for uptake in aquatic biota (Black and McCarthy, 1988). Due to their hydrophobic nature, organic substances have a considerable tendency to interact with organic substances/matter in water. This interaction results in a chemical complex which is too large to permeate through biological membranes and thus unable to be absorbed. It is believed that only the fraction of chemical in "free solution" is available for uptake in aquatic biota. This study investigates the bioconcentration of chlorinated organic chemicals in fish under field conditions.

Goldfish were deployed in cages for 42 days in Little River, Windsor, Ontario approximately 100 m downstream of a municipal sewage outfall. Suspended solids at this site were typically very high but variable and ranged from 5 to 1400 mg/L. Fish were sampled at predetermined intervals, prepared for gas chromatography by solid-liquid extraction techniques and analyzed for over 50 halogenated compounds by electron capture detector. Water samples were obtained at the same time intervals as fish samples and were analyzed for total organic chemical content by liquid-liquid extraction procedures and GC-ECD, and for freely dissolved organic chemical by a novel air sparging technique and GC-ECD. Based on the work of Yin and Hassett (1986), who proposed air sparging as a possible method to distinguish between freely dissolved and "sorbed/codissolved" chemical in the water phase, we have developed a continuous flow gas sparger (Sproule et al., 1991). This instrument has the potential to make measurements of freely dissolved chemical concentrations of very dilute solutions (i.e. typical for hydrophobic chemicals under natural conditions), by removing specifically dissolved chemical from water and leaving the sorbed fraction.

Total water (sorbed + dissolved) chemical concentrations and free water (dissolved) chemical concentrations exhibited similar trends over time with free water concentrations consistently lower than total concentrations. Dissolved chemical concentrations were less than total water concentrations by a factor of 2 to 100. Goldfish bioconcentration factors calculated using total water concentrations underestimated theoretical BCF's based on the BCF-K_{ow} relationship. This suggested that less organic chemical was available for uptake in the fish than was indicated by the total water chemical concentration. BCF's calculated using the dissolved chemical concentration in Little River water somewhat overestimated the theoretically derived values. This overestimate was explained by suggesting food as an additional route of chemical uptake in these fish. It was determined that over 99% of the 1,2,3-trichlorobenzene and 63% of the octachlorostyrene present in Little River at the time of this study was bound to particulate and/or dissolved organic matter in the water column and not available for uptake in field deployed fish. It was concluded that the dissolved chemical concentration in water was more important than total water chemical concentration in chemical uptake in fish.

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AP3

TILLAGE AND EVENT BASED SOIL AND PHOSPHORUS LOSS

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EXECUTIVE SUMMARY

Rainfall simulation experiments were carried out over a three-year period on a range of soil types, slope positions, tillage systems, and times of the year. Standard rainfall simulations used a low and high rainfall intensity on a small 1 m x 1.6 m plot. Measurements included runoff volume and rate, time to ponding (5% area), total soil loss, sediment concentration, texture and sediment P concentration, and surface runoff water velocity. Detailed measurements were also made of soil physical, chemical, and hydrologic properties.

The sites were selected from the existing Tillage-2000 farm sites. Tillage-2000 is a 5 year project sponsored by the Ont. Ministry of Agric. and Food, and the Dept. of Land Resource Science, Univ. of Guelph. The program established field scale tillage treatments on 30-40 farms in 1985 on a wide variety of Ontario soil and landform types. This project made use of these existing tillage plots eliminating the costly field work to establish such plots. The simulation sites were topographic soil landform benchmarks which have monitored for a variety of soil and crop characteristics over the last 5 years. Since the tillage treatments were established at a field scale there was ample room to select good rainfall simulation sites which are quite destructive, and disturb both the soil and growing crop.

In addition to the standard rainfall simulation on small 1 m x 1.6 m plots, a new rainfall simulator was constructed which allowed the spatial scale of the rainfall simulation to change. The simulator consisted of a series of rainfall simulation nozzles each with an electric solenoid valve allowing them to be individually turned on or off. The simulator was used to obtain runoff results from plot sizes of 1, 2, 4, 6, 8 and 10 m long (1.6 m wide), at different rainfall intensities. The purpose of these experiments was to examine the influence of spatial scale on measured hydrologic properties and erosion.

Soil hydrologic properties were measured using a new surface version

of the Guelph permeameter called the Guelph Pressure Infiltrometer (GPI). The GPI gives measurements of field saturated hydraulic conductivity K_{fs} and the matric flux potential ϕ_m both of which can be used to estimate the time to ponding under constant rainfall conditions. Soil cores were also taken for measurement of saturated hydraulic conductivity and the moisture release curve for pore-size characterization. The hydraulic properties were measured in cooperation with a research project funded by the Agriculture-Canada Soil and Water Environmental Enhancement Program - Technology Evaluation and Development (SWEEP-TED).

At a long-term (8 yr) site, comparison of no-till and moldboard plow across a range in soil textures, indicated consistently that the no-till resulted in higher soil bulk density, lower total porosity, lower macroporosity, shorter time to ponding, lower matric flux, lower field saturated hydraulic conductivity, lower saturated hydraulic conductivity, lower infiltration rates (simulation) and higher runoff (simulation). Even though the runoff was higher in the no-till, the total soil loss and phosphorus loss was lower. These effects were consistent across measurements taken in the fall, spring, and summer, and different slope positions.

Similar results comparing total soil loss from the no-till versus both minimum and moldboard were obtained for other Tillage-2000 sites, but the comparison of minimum-moldboard was less clear with no consistent trends. In all of the experiments the controlling influence of the measured (and predicted) time to ponding was obvious, especially if a fixed rainfall simulation time was used and only total (not steady-state) measurements of sediment and water runoff made.

Total phosphorus loss was largely controlled by total sediment loss which was always higher in either the moldboard or minimum till systems compared to no-till, for the high rainfall intensity. For low rainfall intensities, phosphorus and sediment loss in the no-till was often as high or higher than either the minimum or moldboard treatments. The difference in phosphorus loss as a function of rainfall intensity is related to the measured and predicted time to ponding, which was almost always shorter in the no-till. Thus, at low rainfall intensities, it was more difficult to measure runoff and thus phosphorus loss on the no-till, than on the other tillage systems. Depending on the length of time of simulation, then, it was possible to measure more, the same, or less phosphorus loss in the no-till compared to other tillage systems. The steady-state sediment concentration, sediment transport, and phosphorus loss was almost always higher in the moldboard, but since the runoff process started later than the no-till, the total phosphorus and soil loss ratio between the two tillage systems would depend on the time of the rainfall simulation.

The enrichment ratio of phosphorus was significantly correlated to the enrichment ratio of clay, as expected. There were no consistent differences in the enrichment ratios for the tillage systems. However, no-till tended to have slightly higher (20%) values. The main factor controlling enrichment ratios was the surface % clay content of the source soil. A relationship derived from a single site with a wide variation in % clay gave reasonable values for the other sites.

All of the measurements taken were significantly affected by the scale of the measurement technique. The steady-state infiltration rate, a parameter usually considered as a constant for a particular location, varied consistently as a function of rainfall intensity. This was attributed to spatial variability of the surface hydraulic parameters. Runoff water velocity also varied as a function of spatial scale, as did sediment concentrations and phosphorus loss. Phosphorus concentration in the runoff water (ortho-phosphorus) and in the sediment changed as a function of time during the runoff process, with the no-till less affected than other tillage systems. Thus, the relative phosphorus loss comparison between tillage systems depended on the length of time of the runoff simulation.

The experiments indicate a very severe limitation on the use of rainfall simulation to obtain the relative and absolute values of soil losses, runoff losses, or agriculture chemical losses. Depending on the rainfall intensity, or spatial scale (size) of the simulation it is possible to obtain more, equal, or less losses in a no-till system compared to conventional system. Thus, unless the simulations and measurements are made at a number of time and space scales, the data is not very useful for extrapolation. What appears to be very useful, however, is the measurements of the surface hydraulic properties and their variability. They explain a lot of the rainfall intensity dependence of the infiltration rate as well as the runoff volume. Rainfall simulations carried out for fixed time periods, and intensities, with only measurements of total soil loss and total water loss are next to impossible to interpret unless auxiliary measurements on hydraulic properties are also made. Large systematic differences in hydraulic properties as a function of crop row position further complicate the problem. Runoff plot sizes that are not large enough to cover plant row spacing will be significantly affected by where the plot is located, and how much row versus interrow area is included in the plot. For example, a 1 m wide simulation plot automatically is biased for any sites other than 1 m corn row spacings. This is because the runoff area will not have the correct proportion of row and interrow area.

The spatial and temporal dependence of the measurements made in this report suggest that an accurate process based model for prediction of erosion/runoff is not likely to be available for some time. The fact that even on a 1 m x 1 m plot, the infiltration rate varied as a function of rainfall intensity is disturbing. It suggests that the variability of K_s at very local scale is controlling surface runoff generation. By corollary, the variability of K_s at a very local scale must be included into a process based model for accurate runoff predictions. It is highly unlikely that this type of measurement detail will be available for general prediction purposes.

The data also indicate that prediction of the movement of soluble chemicals by runoff will have to take the approach used by Ahuja and co-workers. The process based models for movement of chemicals into the runoff water, however, require an understanding of the temporal changes in the chemistry at the very surface of the soil, a location where measurements are very difficult to obtain. The difference in the temporal distribution of ortho-phosphorus concentrations in runoff water between no-till and moldboard were directly related to the convective versus diffusive flux occurring at the soil surface. Experiments indicated that it is highly likely to get increased ortho-phosphorus flux from a no-till system when the overall infiltration is very low (ie: heavy texture soils). The increased diffusive flux of soluble phosphorus out of the soil coupled with low convective flux away from the surface, and high runoff would result in significantly higher ortho-phosphorus loss. In coarse textured soils the convective flux of chemical away from the surface dominates and masks the effect of tillage, with both tillage systems having low flux.

AP4

BIAS DUE TO SAMPLING GROUNDWATER AND SURFACE WATER FOR TRACE ORGANIC CONTAMINANTS

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In sampling natural waters for trace organic contaminants, positive and negative sampling errors can arise. Positive errors result from desorption or leaching of contaminants from sampling equipment surfaces, whereas the processes responsible for negative errors are volatilization and sorption. Compounds with large air-water partition constants (Henry's law constants) tend to escape into the atmosphere or into sampling bottle head-space, whereas compounds with low water solubilites tend to be sorbed by well-casing and sampling equipment materials. The first source of bias was evaluated by using a series of organic compounds having a range in Henry's laws constants and using various sampling devices. The compounds and their Henry's law constants (atm m^3 / mol) are [1]: methane, 0.676; 1,1-dichloroethene, 0.19; trans-dichloroethene, 0.067; trichloroethene, 0.0091; toluene, 0.0067; benzene, 0.0055. The following sampling devices were evaluated: a double check-valve stainless steel bailer, a peristaltic pump, WaTerra inertial lift pump, IEA syringe sampler, Well Wizzard bladder pump, and Solinst double-valve purge/sample pump. Samples were collected from an artificial well reservoir containing CO_2-charged water which strongly degassed during sampling. The experiments were performed at two concentration levels. Five replicate samples were taken with each sampling device and from a control port at the bottom of the well. The percentage losses were calculated relative to the controls and analysed by nonparametric one-way analysis of variance, i.e. Tukey box plots [2].

The results are depicted in Figure 1. The percentage losses were generally small; the median loss for the high concentration level was 7%, and that for the low concentration level was 1%. The median loss for methane was significantly greater than the median losses for the other compounds, and methane also showed more variability. The methane losses were significantly correlated with the CO_2 losses, and the order of increasing loss among the compounds approximately corresponds to the order of increasing Henry's law constant. These facts suggest that volatilization is the process responsible for the losses, and that volatilization can be expected to produce an unacceptable bias only for compounds which have Henry's law constants greater than 0.2 atm m^3 / mol. The variability associated with sampling device, 4.3%, is smaller than the random error associated with taking replicate samples with a given sampler and comparable to the analytical error associated with replicate determinations on the same sample. In order of increasing median percentage loss, the sequence is: bailer, double-valve pump, bladder, syringe sampler, peristaltic pump, inertial pump. The 95% confidence intervals overlap extensively, so few of the contrasts are significant. The relative performance of the samplers for methane is similar, although none of the contrasts are significant due to the large variance for that compound. The performance of the samplers seems to be consistent with the results of previous studies [2-4], which show that bias tends to increase in the order: grab samplers, positive displacement pumps, suction pumps. The one published evaluation of the inertial lift pump [2] indicated that it performed as well as a bladder pump and better than a peristaltic pump, whereas the present results indicate that it did not perform as well as the other samplers. This apparent discrepancy may be due to operator-induced bias, because it was previously shown [4, 5] that factors such as pumping rate and sample lift height can influence bias.

To evaluate the second source of bias, experiments were performed in which solutions containing ppb levels of chlorobenzenes and chlorobiphenyls were exposed to sampler or well-casing materials for varing lengths of time. The compounds are monochlorobenzene (1-Ben), m-dichlorobenzene (2-Ben), 1,2,4-trichlorobenzene (3-Ben), 1,2,4,5-tetrachlorobenzene (4-Ben), hexachlorobenzene (6-Ben), 2,4-dichlorobiphenyl (2-Pcb), 2,2',5-trichlorobiphenyl (3-Pcb), 2,2',4,4'-tetrachlorobiphenyl (4-Pcb), and 2,2',3,4,5'-pentachlorobiphenyl (5-Pcb). These compounds span a five order of magnitude range in water solubility ($-5 < \log C_S$ (mol/m^3) < 0). Four materials were investigated, polyethylene, poly(tetrafluorethylene) (teflon), poly(vinyl chloride) (rigid PVC) and stainless steel. These materials are commonly used in the construction of surface and ground water sampling equipment.

The concentration versus time curves observed when the solutions were exposed to the polymers were explained using a model for a polymer sheet suspended in a well-stirred solution of finite volume. The relative concentration, C/C_0, is given by [6]

$$C/C_0 = \exp (K^2Dt/A^2) \operatorname{erfc} [(K^2Dt/A^2)^{1/2}] \quad \text{eq 1}$$

where K (dimensionless) is the polymer-water partition coefficient, D (cm^2/s) is the diffusivity of the compound in the polymer, t is the exposure time and A is the solution volume to polymer surface area ratio. The relative concentration vs. log (time) plots for the solutions exposed to the polymers generally conformed to the sigmoid shape predicted by the model. The sorption rate constant, K^2D, which was evaluated by fitting the sorption curves to eq 1, exhibited trends similar to those observed in the previous experiments with low molecular weight aromatic and halogenated hydrocarbons [6, 7]. The sorption rate constant values for polyethylene were considerably greater than those for teflon and rigid poly(vinyl chloride). Also, the values increase among the compounds as the water solubilities decrease and as the octanol-water partition coefficients increase. The K^2D values for the chlorobenzenes and PCB's are therefore generally larger than those for the low molecular weight aromatic and halogenated hydrocarbons in the same polymers. These trends are evident in the log K^2D versus log K_{OW} plots for polyethylene, teflon and rigid PVC shown in Figure 2.

In contrast to the behavior exhibited by the polymers, the relative concentration vs. log (time) plots for stainless steel do not conform to the shape predicted for absorption. Like the halogenated methanes, ethanes and ethenes, it is probable that the chlorinated benzenes and biphenyls were reduced (dehalogenated) while metallic constituents of the stainless steel surface were oxidized. Consistent with this hypothesis, the rate of disappearance was generally observed to be greater for compounds having higher oxidation potentials, i.e. greater numbers of chlorine atoms per molecule. Two of the compounds, 2-Ben and 3-Ben, were not measureably depleted during the 24 hour exposure period, whereas three of the compounds, 6-Ben, 4-Pcb and 5-Pcb, were depleted by more than half. In the previous experiments [6], bromoform and hexachloroethane were depleted by 50 % in approximately 31 days, whereas the other compounds were not depleted during that period. The high disappearance rates observed for the chlorinated benzenes and biphenyls in the present experiments are probably related to the oxidation potentials of the compounds, although the condition of the stainless steel surfaces may also have influenced the rates.

The log K^2D versus log K_{OW} plots can be used to estimate sorption rate constants for compounds having water solubilities within the range spanned by the chlorobenzenes and pcb's. The log K^2D values for the low molecular weight aromatic and halogenated hydrocarbons generally fall below the regression line determined by the chlorobenzenes and pcb's. This may be due to the fact that in the previous experiments, the hypovials were agitated with a tipping shaker at 2 cycles/minute, whereas in the present experiments the hypovials were agitated on a rotary shaker at 400 rpm. In comparing the two methods of shaking, it was found that the K^2D values were about one order of magnitude larger when the hypovials were shaken at 400 rpm. This suggests that diffusion in the liquid phase contributed significantly to the overall mass transfer resistance. Because the absorption model assumes that diffusion in the polymer is solely responsible for the sorption rate, some difficulty would be expected in using this model to predict sorption rates for compounds with very low water solubilities.

It was previously suggested [7] that the absorption model can be used to predict the maximum time that a sample can be exposed to the inner surface of a plastic cylinder, e.g. well casing pipe, before the change in concentration is greater than 10 %. In a typical groundwater monitoring situation, a 1 inch diameter well is encased with teflon or rigid PVC pipe, and the compounds being determined have water solubilities greater than 0.1 mol/m^3. The maximum exposure time for this situation is about 10 hours. Occasionally compounds having much lower water solubilities are determined; some of the organochlorine insecticides and PCB's have water solubilities lower than 10^{-5}. For such compounds, the maximum exposure time to the well casing would be only about 4 s. The maximum exposure time for a sample of surface water held in a 5 l PVC Niskin bottle is 84 s for compounds having water solubilites of order 10^{-5}. The following assumptions were made in estimating the maximum exposure times: the water in the well does not exchange with that outside it after the well is purged; the water in the well or Niskin bottle is well-mixed; and finally, the polymer has not been previously exposed to water containing the organic compounds. Although these assumptions may be violated to some extent in actual sampling practice, the simulations demonstrate that a significant potential for negative sampling bias exists when low solubility compounds are sampled by conventional techniques.

It also possible to estimate the amount of negative bias expected when a plastic tubing is used to remotely sample water at some depth in a lake or aquifer. The model chosen for this simulation is one which describes the loss of heat or concentration of a solute from a fluid that is flowing through a channel or fissure in a matrix of absorbing material. The expression for the time dependence of the relative concentration is [8, 9]

$$C/C_0 = \operatorname{erfc}\left(t_R(K^2D)^{1/2} / 2\Delta(t - t_R)^{1/2}\right) \qquad \text{eq 2}$$

Here, 2Δ is the distance separating the parallel semi-infinite slabs of polymer, t_R is the residence time of the fluid in the channel and K^2D has the same meaning as before. The model assumes that diffusion in the polymer is the rate limiting process and that that longitudinal dispersion (e.g. molecular diffusion of solute in the liquid phase) is negligible. The appropriateness of this model was tested by gas chromatography experiments in which the analytical column was replaced by teflon tubing. The carrier gas flowrate was varied, several lengths and internal diameters of teflon tubing were tested, and several aromatic hydrocarbon vapours were injected. It was observed that the shapes of the breakthrough curves were adequately described by the model. The breakthrough curves also behaved qualitatively in the manner predicted by the model when the diameter and residence time of the tubing was varied. Having thus validated the model, breakthrough curves were calculated for a sampling system often used in research, the Waterloo multilevel piezometer system. It was assumed that the water was pumped through a 5 m length of 1/16 " ID Teflon tubing at a flowrate of 20 mL/min, giving a residence time of approximtely 30 s. The breakthrough curves display a considerable range in the minimum flushing time needed to attain an instantaneous relative concentration of 0.9 when the sorption rate constant value is varied over the range exhibited by the experimental compounds. At a log $\underline{K}^{2}\underline{D}$ value of 10^{-3}, the minimum flushing time is 5 hr. Another groundwater sampling device in common use is the reciprocating inertial pump sampler. Here it was assumed that a 5 m length of 1/2 " ID polyethylene tubing fitted with a check-valve at the bottom end is moved up and down, resulting in an average flow rate of 5 l/min. For a $\underline{K}^{2}\underline{D}$ value of 10^{-1} (5-Pcb in polyethylene), the model predicts a minimum flushing time of 30 min. If mass transfer resistance in the liquid phase is significant, the minimum flushing times would be longer than those predicted by the model. These calculations show that significant errors can occur when sampling water for hydrophobic organic contaminants if insufficient time is allowed for equilibrating the transfer line tubing with the water sample.

In view of the potential for encountering for incurring significant negative bias when sampling hydrophobic and halogenated organic compounds using sampling equipment constructed from synthetic polymers or stainless steel, and of the difficulty of accurately predicting the magnitude of the errors in sampling situations, the following precautions are suggested: i) Sampling equipment and procedures are used which minimize the area and time of exposure to synthetic polymers and stainless steel, ii) Soft polymers, such as flexible PVC and polyethylene are avoided, and iii) Tests are conducted to ensure that representative samples are be obtained.

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Figure 1. Tukey box plots of percentage loss (N=108).

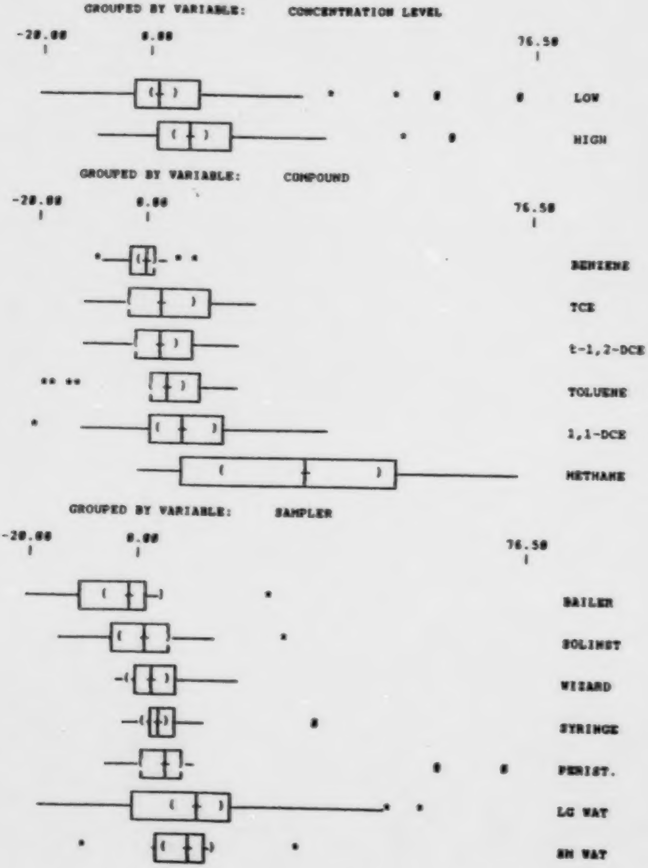
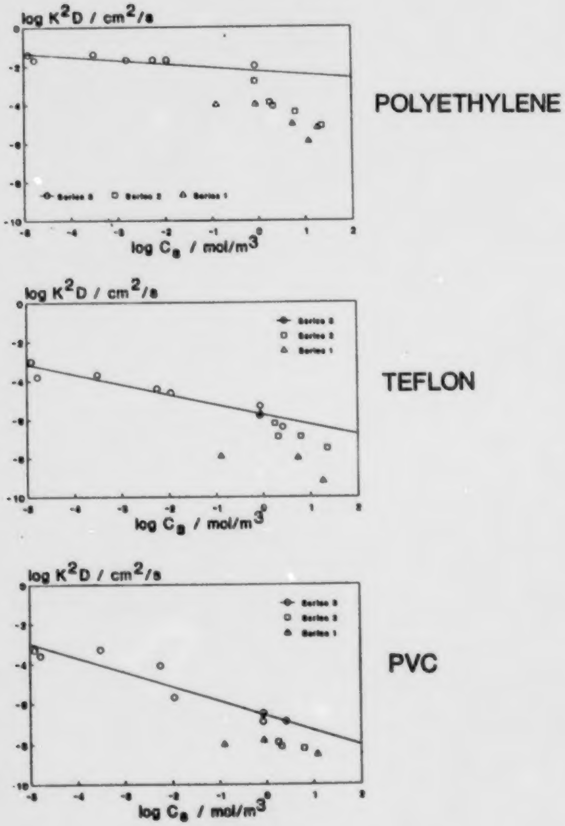


Figure 2. Log K^2D versus log C_S plots for polyethylene, teflon, and rigid PVC. Series 1 and 2 data are for the low molecular weight halogenated and aromatic hydrocarbons, respectively [6, 7]. Series 3 data are for the chlorobenzenes and PCB's. The regression lines for Series 3 data are indicated.



AP5

DETERMINATION OF GEOCHEMICAL MODIFICATION OF GROUNDWATER ENTERING SURFACE WATERS.

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Many disposal sites are on lands contiguous with surface waters. Contaminants can be transported by groundwater from these sites. A biogeochemical transition zone exists at, or very near the sediment/water-interface through which groundwaters seep. Our objective is to investigate conditions under which contaminant flux to surface water may be controlled by reactions within this transition zone.

In this work, controlled tests were run in large seepage tanks to quantify the interactions of contaminated groundwater with the sediments through which discharge occurs. To compare predictions made from standard piezometric sampling with the actual contaminant flux to surface water, measurements were made in the groundwater, the surface water and at various depths below the surface-water/groundwater interface. The groundwater was artificially contaminated with nickel, cobalt, lithium, bromide, sulfate and nitrate. The water at the bottom of the tanks was virtually devoid of oxygen and the surface water above the sediment was agitated with air bubbles to maintain oxygen saturation.

Initial runs showed that major ions Na, Mg, K, Ca, and Cl behaved conservatively and mass balances were very good. Therefore, the seepage tank approach gives a quantitative framework for contaminant testing. By day 30 of the contaminant injection experiments, it was apparent that lithium was not conservative, contrary to indications in the literature. It was apparent too that nickel and cobalt were more reactive than lithium. Cation analyses (Fe, Mn, Co, Ni, Li) for days 51 and 112 are due three weeks from this writing. Glass slides, emplaced across the sediment/water interface, will be analyzed for metal oxyhydroxide coatings, which are now visible on the sediment surface.

Discharges of groundwater-borne contaminants are increasingly viewed as potential sources of surface-water contamination. This work is needed to provide experimental data for testing models for contaminant transport across discharge zones. Future work will focus on phosphorous behaviour, particularly under anaerobic conditions, and on the behaviour of selected metals under acidic conditions.

AP6

IMPACT OF LIVESTOCK MANURE AND FERTILIZER APPLICATION ON NITRATE CONTAMINATION OF GROUNDWATER.

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Livestock production is a major agricultural activity in Ontario. The livestock population of Ontario in 1987 would produce 3×10^7 tonnes of excrement. The N, P and K replacement value of the nutrients contained in this manure is $158 million. Livestock wastes have traditionally been returned to land from which the major portion of the livestock feed was produced. As agricultural specialization has increased, there has been a tendency toward a separation of livestock and crop production. Currently much of the poultry and swine production and an increasing amount of beef production are concentrated on a minimal land base. Feed is imported from considerable distances. As a result of specialization, livestock wastes are applied to smaller and smaller land areas. Although the fertilizer replacement value of the manure is significant, in many cases the cost of transportation outweighs the value. At this point, disposal of the manure rather than utilization becomes the objective and there is little concern for the effect of rate, timing or method of application on the availability of the nutrients or their use by the crop and hence environmental concerns arise.

Of particular concern is the potential impact of excessive manure application on the concentration of NO_3^- in groundwater. There are a number of isolated measurements of elevated groundwater NO_3^- concentrations in Ontario that are attributable to application of nitrogen, either as manure alone or in combination with fertilizer N. The concern for NO_3^- in water arises primarily from a threat to infant health. A safe limit of 10 mg NO_3^--N L^{-1} has been established for drinking water.

The Agricultural Code of Practice for Ontario was designed, in part, to reduce the impact of livestock wastes on water quality to acceptable levels. The Code of Practice established minimum land areas for livestock operations based on the nitrogen in the manure. Manure-N application rates twice that required by the crop are permitted. This assumes that only half the nitrogen present in the manure would be available to the crop in the year of application. While this may be an acceptable limit for a single year, continued application at this rate may not be acceptable.

In spite of the acknowledged potential for impact of livestock manure on water quality, only limited research has been conducted on this problem in Ontario. With the major increase in concern for NO_3^- in groundwater, it is imperative that increased effort be devoted to assessing and reducing the impacts of livestock wastes. Maximum environmentally acceptable application rates[1] for fertilizer and livestock manures must be defined for a variety of nitrogen sources and soil types. These maximum rates must be based on field studies examining nitrate movement below the root zone.

Evaluation of potential nitrate movement into groundwater is complicated by the potential for denitrification in the sub-soil, a process whereby NO_3^- is converted to gaseous nitrogen oxides and ultimately nitrogen gas. This is particularly true of organic nitrogen sources such as livestock manure where both nitrogen and carbon are being added to the system. The addition of carbon increases the potential for denitrification and therefore moderates the nitrate leaching potential. The extent of sub-surface denitrification as a function of manure type, soil type, time of application and depth to groundwater has not been assessed. This information is important to the determination of maximum environmentally safe application rates of manures and fertilizers.

The objectives of this work are:

1. To determine the amount of NO_3^- and dissolved organic carbon leaving the root zone as influenced by nitrogen source and rate of application.

2. To establish the effect of time of manure application on crop response and NO_3^- movement to the groundwater.

3. To evaluate the potential for denitrification at several soil depths in relation to dissolved organic carbon and NO_3^- transported from the root zone.

The study, located at the Elora Research Station, examines three nitrogen sources (ammonium nitrate, solid beef cattle manure and liquid dairy cattle manure), at three rates of application (0.5 x, 1.0 x and 1.5 x recommended rates based on spring soil NO_3^- test) and at two times of application (spring and fall). Monitoring of porewater nitrate concentration at 75 cm depth is combined with a detailed study of solute transport to evaluate nitrate movement to groundwater. Major processes of the nitrogen cycle will be monitored by measuring biomass C and N, mineral N, and dissolved organic carbon at four soil depths (0-15, 15-30, 30-45 and 45-60 cm). Denitrification potential is being examined in soil samples from three depths (10, 20 and 40 cm) on plots receiving the highest rates of N application.

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[1] The maximum environmentally acceptable rate of nitrogen application is that which will ensure that the annual volume-averaged NO_3^- concentration in water leaving the root zone does not exceed a set concentration

AP7

HYDROGEOLOGY OF AN UNCONFINED SAND AQUIFER AND ITS EFFECT ON THE BEHAVIOR OF NITROGEN FROM A LARGE-FLUX SEPTIC SYSTEM

by

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Abstract

Detailed monitoring of groundwater in a shallow sand aquifer impacted by a large-flux septic system showed that water quality in the shallow water table zone below the tile bed was similar to that of smaller-flux septic systems in similar hydrologic settings where effluent residency in the unsaturated zone was of similar duration. During residency of about one week in the 4-m thick unsaturated zone, effluent NH_4^+ was largely oxidized to NO_3^-, about 75% of DOC was biodegraded, and acidity produced by the above reactions was neutralized by dissolution of calcite. Beneath the tile bed and extending laterally downgradient a distance of 80 m to the Lake Erie shoreline, a distinct plume of impacted groundwater was easily distinguished by elevated levels of electrical conductance, Cl^-, NO_3^-, HCO_3^-, Na^+, Ca^{2+}, and K^+ and by depressed levels of pH and dissolved oxygen. High NO_3^- levels that occur below the tile bed disappear, however, in the anaerobic plume core zone 10 to 70 m downgradient, apparently as a result of denitrification. The rich reserve of solid-phase organic carbon in the aquifer sediment (2.5%) probably provides much of the organic carbon for heterotrophic denitrification. This condition is in contrast to other septic system plumes in sand aquifers where high NO_3^- levels persist and where aquifer organic carbon values are much lower. Although NO_3^- is attenuated in the plume core, persistence of NO_3^- along the aerobic upper fringe of the plume demonstrates the ability of septic systems to cause significant water-quality degradation of sand aquifers when the conditions favorable for denitrification do not exist.

The sharp boundary between the plume water and non-impacted water adjacent to and overlying the plume in the area 50 to 100 m downgradient from the tile bed, and the undiluted nature of non-reactive solutes such as Cl^- throughout the core of the plume, demonstrates that dispersion has only a weak influence on the plume. This is consistent with dispersion studies in many other sand aquifers.

INTRODUCTION

In 1986, the groundwater research group at the University of Waterloo began studies of the impact of conventional septic systems on unconfined sand aquifers. This research encompasses single-family septic systems, larger multi-user septic systems, and large aeration ponds. These systems have several features in common: the effluent is domestic rather than industrial; the effluent infiltrates directly downward from the distribution tiles or pond bottom through unsaturated sand to the water table, which varies in depth from 2 m to 15 m; below the water table, the effluent causes a contaminant plume which extends laterally in the aquifer toward the discharge area; and the plume at each site is easily delineated by the monitoring of mobile and relatively non-reactive effluent constituents such as Na^+ or Cl^-. At each site, the plume has been monitored in exceptional detail by means of networks of single-hole multi-level piezometers or samplers of the type described by MacFarlane et al. (1983) and Mackay et al. (1986).

This paper describes one of these studies, a septic system at a campground in a seasonal use public park on the north shore of Lake Erie in the

Province of Ontario. The site is referred to as the Long Point site, after the name of the provincial park. The purpose of the study is to determine the behavior of the nitrogen species, NH_4^+ and NO_3^-, in the groundwater zone below such a larger flux septic system and to evaluate geochemical conditions in the plume affecting their behavior.

In septic-system effluent, nitrogen is an important constituent because it typically occurs in the concentration range of 20 to 60 mg/L (expressed as N). The maximum safe limit for NO_3^- specified for drinking water in North America and Europe is 10 mg/L (as N). Of the various constituents from septic effluent found in groundwater, NO_3^- is most commonly above the drinking water limit. NO_3^- is formed by oxidation of effluent organic nitrogen and NH_4^+ during travel through the unsaturated zone. Dispersion in sand or gravel aquifers generally causes little attenuation of NO_3^-; therefore, NO_3^- undergoes little dilution with ambient groundwater. Denitrification, whereby NO_3^- is transformed to N_2 and in uncommon circumstances to N_2O or NH_3^+, is the process of greatest potential to diminish NO_3^- in plumes. For denitrification to occur, the plume must be anaerobic and, in the plume, there must exist an adequate energy source for the bacteria that facilitate the denitrification process. A preliminary study of the Long Point plume indicated that denitrification was likely taking place in the plume, subsequently, a more detailed investigation was directed at the cause and geochemical effects of denitrification in the aquifer.

Long Point Provincial Park is located at the west end of Long Point, which is a narrow sand spit extending 30 km eastward into Lake Erie from near Port Rowan, Ontario. The main campground, which is open from April to November, has about 200 overnight camping sites and is serviced by a single comfort station containing toilets, showers, and facilities for clothes laundering. Since 1971 or earlier, effluent from the comfort station has been released to a conventional septic system tile bed by a water level-activated pump. Potable water usage in the park is about 50 m^3/day during the July and August peak, whereas only about 10 m^3/day is used during the spring and fall.

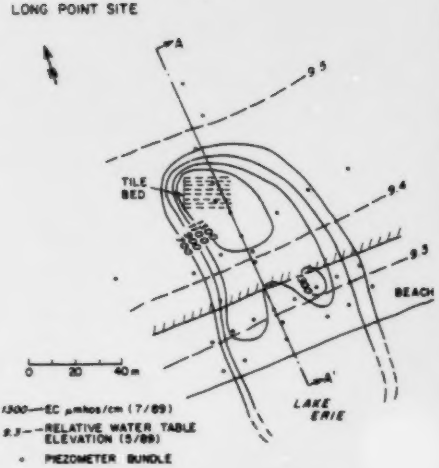

Figure 2. Vertically averaged groundwater electrical conductance and water table configuration in the surficial aquifer.

Hydrostratigraphy and Solid-Phase Properties

The six sediment cores taken along section A-A' showed that the surficial aquifer of permeable lacustrine sand extends to 5-10 m depth and overlies a continuous aquitard of clayey lacustrine silt (Table 1; Figure 3). The erosional contact between the two units is sharp and flatlying. The aquifer is relatively homogeneous, although several silty to pebbly sublayers can be traced between cores. The upper part of the aquifer has been reworked by wind. Sand lenses were also identified within the aquitard at the bottom of cores 24 and 33.

The aquifer solids properties given in Table 1 show that the aquifer is permeable (hydraulic conductivity (K) = 2×10^{-2} cm/s) and is rich in carbonate minerals (18.5 wt% $CaCO_3$ equivalent). Sulphur content averages 0.02% of the sediment dry weight. The solid-phase organic carbon content of the aquifer (2.5%) is an amount that is much larger than values reported in the literature for other unconfined sand aquifers in Ontario. The high organic carbon and significant sulphur values in the Long Point aquifer

Table 1. Sediment solid phase properties

		Aquifer (N=10)	Aquitard (N=2)
gravel (> 2 mm)	wt %	0	0
sand (2-0.063 mm)	|	99	28
silt (0.063-0.002 mm)	|	1	63
clay (<0.002 mm)	|	< 1	9
carbonate ($CaCO_3$ equiv.)	|	18.5	
organic carbon	|	2.5	
sulphur	|	0.02	
hydraulic conductivity¹ (cm/s)		$2x10^{-2}$	2x10[illegible]

1) From grain size data using Hazen formula

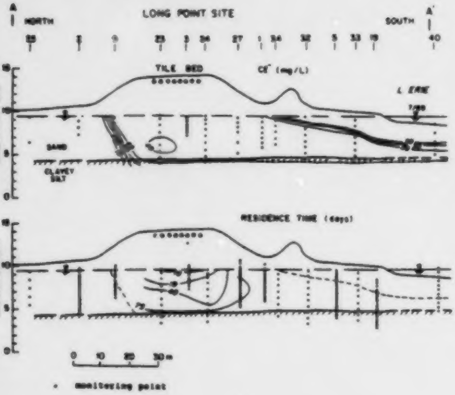

Figure 3. Cl⁻ distribution (top) and groundwater residence time (bottom) along the plume centreline.

probably originated at the time of deposition in a near-shore lake environment that encroached on, or alternated with, wetlands. As discussed below, the organic carbon and sulphur contents of the aquifer probably exert a strong influence on geochemical processes in the plume.

GROUNDWATER FLOW

The average hydraulic gradient observed along section A-A' (0.002, Figure 2) and the mean hydraulic conductivity (K) of the aquifer (2×10^{-2} cm/s, Table 1) indicate, from the Darcy equation, that the horizontal groundwater velocity in the aquifer is on the order of 35 m/a in the area of the tile bed, and that travel time from the tile bed area to the Lake Erie shoreline is about 2-3 years. In the velocity calculation, a value of 0.35 was assumed for the effective porosity. This value is typical of surficial lacustrine sand deposits in Ontario.

A second estimate of groundwater velocity and residence time in the area below the tile bed was provided by the bromide tracer test. NaBr injected during the peak-use period resulted in maximum measured Br^- concentrations of 92 mg/L in the tile effluent and 40 mg/L at the water table below the tile bed. The background level of Br was <0.5 mg/L. Figure 3 (bottom) shows the position of peak Br^- concentrations, 10, 19, 40, and 75 days after injection. The test showed that average effluent residency on the septic tank was on the order of 1 to 2 days and then about 7 days in the 4-m thick unsaturated zone below the tiles. Vertically downward flow was demonstrated in the groundwater zone below the tiles, where the tracer slug reached the bottom of the aquifer after 75 days.

PLUME CHARACTER

A distinct plume of septic system-impacted groundwater was found to emanate from the tile bed area. The plume has a uniform width of about 60 m and extends 80 m from the tile bed area to the Lake Erie shoreline, where it discharges at some unknown distance offshore (Figure 2). The plume waters were easily distinguished in the field by elevated levels of EC (1100 to 1500 µmhos/cm) reflecting higher average concentrations of Cl^- (46 mg/L), Na^+ (37 mg/l), HCO_3^- (229 mg/L), Ca^{2+} (190 mg/L), K^+ (18 mg/L) and in the area below the tile bed, higher NO_3^- (51 mg/L as N) and PO_4^{3-} (2.3 mg/L as P) (Table 3; Figures 2, 3, 5, 6,   ). Generally, about 80% of the nitrogen in septic system effluent occurs as inorganic N (NH_4^+ + NO_3^-), which is typically in the concentration range of 30-111 mg/L (Walker et al., 1973; Viraraghaven and Warnock, 1975; Andreoli et al., 1979); therefore, inorganic N levels observed in the effluent at Long Point and in the plume core below the tile bed appear typical of most domestic effluents. The plume waters were also characterized by slightly depressed pH levels (6.5 to 6.8) and slightly increased DOC levels (5 mg/L) compared to background values (Table 3)   . Except along the upper fringe, dissolved oxygen was low or absent within the plume, although background groundwater also had low DO at depth (Figure 6). Chloride distribution along the plume centerline (Figure 3) showed that, in the area below the tile bed, the plume encompasses the entire 5 m saturated thickness of the aquifer. In the downgradient area below the Lake Erie beach, however, the plume becomes overlain, as the shoreline is approached, by an increasingly thick lens of non-impacted groundwater. This lens is a result of storm wash which periodically engulfs the beach area and has the effect of greatly increasing the water table recharge rate in that area.

Table 3. Major ion geochemistry, Long Point plume.

	Background[a] (N=3)		Effluent[b] (N=6)		Plume Core[c] Below Tile (N=8)		Plume Core[d] 48-70 m Downgradient (N=6)	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
Cl mg/L	6	5	44	17	46	6	44	1
SO_4^{2-} mg/L	20	6	26	5	34	25	78	19
PO_4^{3-}-P mg/L	0.02	0.01	6	1	2.3	2.6	0.02	0.006
alk (as HCO_3) mg/L	98	26	282	17	229	29	231	19
NO_3-N mg/L	0.8	0.6	1	1	51	17	5	12
NH_4^+ mg/L	0.2	0.1	66	10	1	1	9	7
Ca^{2+} mg/L	60	12	77	13	190	17	163	19
Mg^{2+} mg/L	8	1	13	1	16	4	20	7
Na^+ mg/L	2	2	35	6	37	6	36	1
K^+ mg/L	1	0.6	17	7	18	6	17	8
DOC mg/L	2.7	0.8	21	6	3.0	0.8	3.2	0.2
pH	6.9	0.2	7.2		6.6	0.08	6.7	0.05
N/Cl			1.5		1.1		0.3	
EC umhos/cm	430				1390		1200	

[a] Piezometer bundles 25 depths, 1 and 4 m; 33 depth, 1 m; 7/89

[b] Effluent from sampling the [illegible] tank; 7/89-6/90

[c] Piezometer bundles 23 depths 4.9, 5.6, and 7.0 m; 24 depths 5.1, 5.6, and 7.0 m; 3 depths 4.7 and 5.6 m; 7/89

[d] Piezometer bundles 32 depths 4.1 and 5.5 m; 33 depths 3.6 and 5.0 m; 34 depths 4.4 and 5.8 m; 7/89

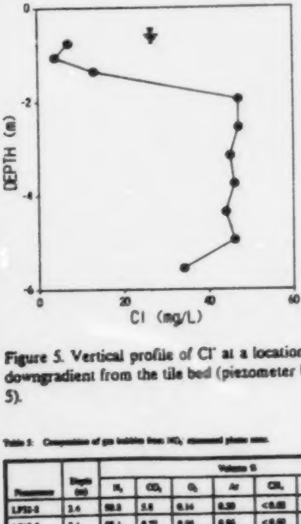

Figure 5. Vertical profile of Cl⁻ at a location 48 m downgradient from the tile bed (piezometer bundle 5).

Table 5: Composition of gas bubbles from NO_3^- saturated plume zone.

Piezometer	Depth (m)	Volume %						
		N_2	CO_2	O_2	Ar	CH_4	N_2O	C_2H_6
LP30-8	3.6	98.8	1.8	0.14	0.30	<0.03	<0.01	<0.01
LP13-6	3.1	98.1	0.77	0.95	0.86	<0.03	<0.01	<0.01
LP5-11	3.8	96.7	2.4	0.90	0.50	<0.03	<0.01	<0.01

The boundary between the plume and the adjacent non-impacted waters is abrupt both vertically and laterally, and non-reactive solutes such as Cl⁻ remain almost undiluted from effluent values even in the downgradient areas (Table 3; Figures 2, 3, and 5). The abrupt interface indicates that the sand aquifer has only a weak capacity to cause dispersion in any direction. Figure 5 shows that, at a location 48 m downgradient from the edge of the tile bed (piezometer bundle 5), Cl⁻ values along the upper boundary of the plume change from an essentially non-impacted value of 13 mg/L at 1.3 m depth to a plume value of 44 mg/L at 1.9 m depth. Similarly, sharp Na+ gradients observed along the top of the Cambridge septic system plume were used to ascertain, using calibrations of mathematical models, a value of vertical transverse dispersivity for the Cambridge aquifer of on the order of 10^{-3} m (Robertson et al., 1991; Shutter et al., 1991). The Long Point aquifer appears to have a similarly small value of vertical transverse dispersivity. Large-scale natural gradient tracer tests in unconfined sand aquifers (Sudicky et al., 1983; Freyberg, 1986; Garabedian, 1987; Moltyaner and Killey, 1988 a,b) and detailed mapping and modeling of plumes from municipal landfills on such aquifers (Frind and Hokkanen, 1987; Frind and Molson, 1989) are consistent with this finding of weak vertical transverse dispersion.

GEOCHEMICAL PROCESSES

Oxidation in the Unsaturated Zone

A comparison of the effluent and plume core composition (Table 3) and an examination of the major ion profiles below the tile bed indicate that the most important unsaturated zone reactions are: consumption of effluent DOC by a reaction such as:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad (1)$$

where CH_2O represents organic matter and nitrification of effluent NH_4^+ by:

$$NH_4^+ + 2O_2 \rightarrow NO_3 + 2H^+ + H_2O \qquad (2)$$

During midsummer, the effluent DOC level of 28 mg/L decreased to 5 mg/L at the water table, and the effluent ammonium level of 58 mg/L N decreased to < 1 mg/L. This indicates that reactions (1) and (2) were completed largely during the 5- to 10-day residency of the effluent in the 4-m thick unsaturated zone. A similar degree of DOC

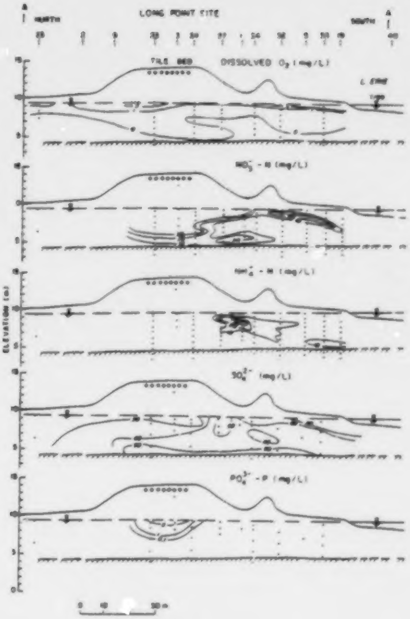

Figure 6. Distribution of dissolved O_2, NO_3^-, NH_4^+, SO_4^{2-}, and PO_4^{3-} along the plume centerline.

oxidation and NH_4^+ nitrification was observed within the sandy unsaturated zones at the Cambridge and Muskoka single-family septic system sites (Robertson et al., 1991; Wilhelm et al., 1991). At the former site, effluent residency in the unsaturated zone was about 10 days, similar to Long Point, while, at the latter site, residency was somewhat longer. Likewise, Walker et al. (1973) reported complete nitrification of effluent NH_4^+ within 1 m in unsaturated sand below a tile line at a septic system in Wisconsin. Reactions (1) and (2) consume oxygen; therefore, the unsaturated zone at Long Point is presumed to be aerobic during midsummer. The observed depletion of groundwater DO and the continued attenuation of DOC levels from values of about 5 mg/L at the water table to near-background values of 3 mg/L at depth suggest that reaction (1) continues below the water table.

Acidity is produced by NH_4^+ nitrification (Equation 2) and indirectly from CO_2 produced by DOC consumption, i.e.:

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \qquad (3)$$

so that depressed pH levels (6.5) are observed at the water table. Significantly increased Ca^{2+} levels observed at the water table, however (190 mg/L vs. the effluent value of 77 mg/L; Table 3), suggest that much of the acidity is buffered in the unsaturated zone by calcite dissolution:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (4)$$

Groundwater Zone

Geochemical speciation modeling using a revised version of the computer code PHREEQE (Parkhurst et al., 1980) suggests that the plume waters maintain a condition of near-saturation with respect to calcite as log saturation indices (SI) for calcite vary within a narrow range close to zero (-0.32 to 0.11).

The shallow water table zone below the tile bed is supersaturated with respect to hydroxylapatite ($Ca_5OH(PO_4)_3$) with log SI values in the range of 0.76 to 0.99 observed. The abrupt attenuation of the PO_4^{3-} plume at a depth of 2 m below the water table (Figures 6) is thus possibly the result of a mineral precipitation reaction, particularly since the zone of PO_4^{3-} attenuation is also a zone where pH and Ca^{2+} concentrations increase along flowpaths. Both of these factors would decrease hydroxylapatite solubility. A similar condition of PO_4^{3-} distribution and attenuation was observed at the Cambridge septic system site also located on carbonate-rich sands (Robertson et al., 1991; Wilhelm et al., 1991). PO_4^{3-} is generally highly attenuated in subtile sediments (Sawhney and Starr, 1977; Jones and Lee, 1979); thus, PO_4^{3-} behavior at Long Point appears typical.

DENITRIFICATION

Almost complete disappearance of NO_3^- (to <0.5 mg/L-N) occurs in the plume core 10 to 70 m downgradient from the tile bed (Figure 6) and at the bottom of the aquifer in the area below the tile bed. These zones of nitrate loss correlate closely to the zones of low (<0.3 mg/L) or absent DO. This is demonstrated most vividly in the downgradient area where NO_3^- persists at concentrations > 20 mg/L-N along the upper fringe of the plume where DO levels are >0.3 mg/L. The correlation between low NO_3^- and a deficiency of oxygen suggests that NO_3^- is being lost due to denitrification. Denitrification normally occurs through a series of microbially mediated steps whereby NO_3^- is reduced to N_2, which occurs in the water as dissolved gas and aqueous N_2 (Delwiche, 1981). The composition of exsolved gas bubbles from the NO_3^- attenuated zone was more than 90% N_2 (Table 5), further implicating denitrification (Vogel et al., 1981). The small amount of O_2 detected in the gas bubbles (0.1 to 0.9%) was probably the result of sampling error as dissolved O_2 was known to be depleted in this plume zone (Figure 6). In anaerobic environments where labile organic carbon is available as an electron donor, the reaction is catalysed by heterotrophic bacteria and can be simplified to (Delwiche, 1981):

$$5CH_2O + 4NO_3^- \rightarrow 5CO_2 + 2N_2$$

$$+ 3H_2O + 4OH^- \qquad (5)$$

This reaction has been used to account for NO_3^- attenuation observed in several anaerobic groundwater environments (Trudell et al., 1986; Smith and Duff, 1988; Starr and Gillham, 1989).

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AP8

PREDICTION OF BIOACCUMULATION OF POLYCHLORINATED BIPHENYLS IN ONTARIO FISH.

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Rasmussen et *al*. (1990) recently developed a model for the prediction of total polychlorinated biphenyls (PCBs) in lake trout as a function of three predictor variables. The model was developed from the Ministry of the Environment Sport Fish Contaminants Monitoring Program and used lake means (n = 1 to 32 fish) of PCB measured in skinless and boneless dorsal fillets (OMOE 1986). Total PCBs were found to be a positive function of both the percent lipid content of the trout and a classification rank describing the food web structure of the lake planktonic community (described below), and a negative function of the latitude of the lake. Although these three predictor variables described a significant fraction of the variability in PCB content ($r^2= 0.74$), significant correlations between the predictor variables make it difficult to rank their relative contributions to the observed lake trout PCB burdens. A major goal of this research was to evaluate the model using the individual fish data in place of the lake means, since considerable within lake variability in lake trout PCB content has been observed. The second goal was to examine the degree of collinearty between the predictor variables by residual analysis, in order to determine which of the predictor variables has the greatest impact on lake trout PCB burden. Another goal was to use the model to predict PCB levels in Lake Ontario lake trout in order to evaluate the contribution of urban and industrial activities.

The lake classification system developed by Rasmussen *et al.* (1990) distributed lakes among 3 classes which describe the presence or absence of pelagic planktivorous fish, such as ciscoes, alewifes, smelt and whitefish, and the presence or absence of the freshwater invertebrate, *Mysis relicta*. Class 1 lakes have relatively simple food webs since neither *Mysis* nor pelagic planktivorous fish are present. In Class 1 lakes, lake trout are planktivorous and feed almost exclusively on the zooplankton, whereas in Class 2 and Class 3 lakes the trout are piscivorous. Class 2 lakes include lakes with pelagic planktivorous fish, but no *Mysis*, and these planktivores feed upon the zooplankton. PCB content of Class 2 lake trout are higher than Class 1 lakes, but less than Class 3 lakes which have a more complex food web. Class 3 lakes include the pelagic planktivorous fish as well the *Mysis* which are the major food item for the planktivores. *Mysis* prey upon the zooplankton and larger phytoplankton, thus there are several food levels between the plankton and the lake trout in Class 3 lakes, and the bioaccumulation of PCBs is the greatest.

Data for 657 individual lake trout from 50 Ontario lakes were used in the analyses. Plots of PCBs as a function of fish length or percent lipid content demonstrated a better fit against fish length. While the Ramsussen *et al.* (1990) means data suggested a better fit using percent lipid, the difference between lipid and length was minimal. Plots of the PCB distribution *versus* lake latitude indicated that northern lakes do have less contaminated fish. However, highly developed lakes in the Muskoka and Haliburton regions at 4500 to 4540 °N (e.g.

Lake of Bays, Muskoka, Lake St. Nora) not only contain fish high in PCBs, but also have had greater sampling effort. This could bias the latitude contribution to the model and needs to be further examined. Identifying the contribution of latitude is important since it may relate to patterns of atmospheric distribution and fallout of contaminants, with lakes furthest removed from the urban centers receiving lower contaminant loading. One means of demonstrating this effect is by plotting different contaminants against one another; for example, the plot of the sum of DDTs against PCBs across a set of lakes has an r^2 of 0.81. Thus lakes high in one contaminant are also high in others, suggesting the atmosphere as a common source. These plots are also useful for identifying outliers, lakes with additional or point source contamination.

The plot of PCB content in lake trout against the lake class rank clearly demonstrates the importance of the structure of the food web. Class 1 lakes are uniformly low in PCBs (< 100 ng/g wet weight), Class 2 lakes are somewhat higher (100 to 400 ng/g ww), while Class 3 lakes contain fish as high as 1600 ng/g ww. However, the range of PCB content of Class 3 lakes is extremely broad and the lower levels are not different from Class 1 or Class 2 lakes.

Two regression models are presented: both relate PCB in lake trout as a function of latitude and class number, and either fish length or percent lipid. The fit obtained with either form of the model was similar, with r^2 equal to 0.50 for the length model and 0.47 for the percent lipid model. Both regression equations were then used to predict the PCB burden of Lake Ontario lake trout, with the result that either version systematically underpredicted PCBs for Lake Ontario trout.

The ratio of DDT to PCB in Lake Ontario is significantly lower than for the other lakes. This observation, together with the model underestimating Lake Ontario lake trout PCB content, suggests that Lake Ontario PCB levels are higher due to alternative sources than what the inland lakes recieve. However, the arithmetic mean PCB in Lake Ontario is not different from the arithmetic mean PCB for Class 3 lakes. This is attributable to a subset of Class 3 lakes identified with very high PCB levels. These results suggest that an alternative predictor variable to explain the wide range of PCB levels in Class 3 lakes would improve the model fit, and may in turn also improve the prediction of PCBs in Lake Ontario lake trout. With suitable refinement, we hope to identify the relative contribution of point source *versus* atmospheric inputs to Ontario lakes. In the past, this was not possible because of the confounding problem of elevated contaminant levels due to trophic structure and latitude.

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AP3

FLOW OF MANURE THROUGH SOIL MACROPORES

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Various studies have linked the spreading of livestock manure to a degradation in the quality of land-drainage water and surface water (e.g. Evans and Owens, 1972; IJC, 1980; MOE and UTRCA, 1984). Land-spreading continues to represent to the farmer the most practical and efficient way of recycling the nutrients and organic matter contained in manure. Unfortunately, even when farmers have followed the advice of printed cropping recommendations or crop consultants, they have sometimes had problems with liquid manure entering field tile drainage systems. This has lead to contamination of surface water.

Dean and Foran (1990) reported on liquid manure spread on a variety of farm fields, at rates ranging from 36 m^3/ha to 140 m^3/ha. Significant contamination of tile drainage water occurred at 8 of the 11 sites. The spreading rate appeared to have little to do with this contamination. The most likely pathway for the manure seemed to be large soil pores (macropores - cracks, channels formed by plant roots or worm, or other relatively large voids in the soil). Priebe and Blackmer (1989) found that preferential flow of water through soil macropores was an important factor affecting N movement in Iowa soils.

Objectives -

1) Determine to what extent flow of manure through soil macropores occurs under typical Southwestern Ontario conditions.

2) Compare the macropore flow for the soil from two tillage systems - no-till versus conventional tillage.

Collection of Soil Columns - A farm was selected that would give the following soil conditions:

a) clay loam soil, no-till
b) clay loam soil, conventional tillage
c) sandy loam soil, no-till
d) sandy loam soil, conventional tillage

Different methods have been tried by researchers to obtain undisturbed blocks of soil. Most of these have used soil depths of only 30 cm or less. The problem addressed by this study involved manure entering drain tiles. Since drain tiles are typically installed at depths of 75 to 90 cm, a means of getting deeper cores was needed. The optimum solution appeared to be the use of 15 cm diameter pipe pressed into the ground using a Meta-Drill machine (Meta-Probe Inc., Picton, Ont.). Fifteen columns were collected for each of the 4 soil conditions listed earlier. Each was about 60 cm deep (average depth = 61.4 cm, std. dev. = 1.9).

Preparation of Soil Columns - As the columns came out of the ground, they were inspected to make sure no soil had fallen out of the bottom end (if soil fell out, the column wasn't used). End caps were fastened to both ends to prevent drying, and the soil was transported to the lab. There, they were stored in a cool dark area for several days (still capped).

The following steps were taken to bring the soil columns to a similar moisture content, as close as possible to Field Capacity[1]. The bottom of each column was wrapped with filter cloth (geotextile) to prevent soil from falling out. The columns were then stood in pails of tap-water. A depth of 37 cm of water was maintained in the pails for several days. The columns were removed from the pails and set on the test rack. The filter cloth was left in place for at least 12 hours and the soil was allowed to dry to Field Capacity.

Applying Manure to Soil - Liquid swine manure was used for the test. Chloride was used as a chemical tracer. Manure was sprinkled onto the soil surface by pouring it through the sprinkler head from a garden watering can. Treatment 1 consisted of a depth of 10 mm of manure. Treatment 2 was double this amount. Treatment 3 consisted of 10 mm of distilled water. Approximately one hour after these treatments were applied, distilled water equal to a depth of 10 mm was added to each of the soil columns.

Effluent Sampling and Analysis - Effluent dripping from the bottom of the columns was collected in plastic bottles. These bottles were weighed at various times (after application of the final amount of water). When the effluent weight exceeded about 30 g, a new bottle was inserted and the sample was capped and refrigerated. After 17 hours, all bottles were weighed, capped, and refrigerated. Where there was in excess of 30 g of effluent in a bottle, a portion was drawn off into sterilized bottles for bacterial analysis. Effluent that had been refrigerated after only one hour (following treatment) was analyzed for levels of fecal coliform, fecal strep. and *E. coli* bacteria. For the remainder of the samples (i.e. those that had remained in the bottles at room temperature for several hours) only fecal coliform levels were measured.

Soil Sampling and Analysis - When the effluent samples were removed, the soil columns were capped and laid on their sides to prevent further downward moisture movement. During the next week, soil samples were taken from each core. The soil column was removed intact from the pipe (the plastic pipes were cut; the soil in the steel pipes was pushed out). Samples of well-mixed soil were taken from five depths.

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[1] Field Capacity - the state in the soil where capillary pores are saturated with water and all the water that will drain by gravity is gone from the soil.

RESULTS AND DISCUSSION

Effluent Volume - The speed at which liquid moved through some soil columns was dramatic. In some cases, liquid began dripping from the columns within two minutes of application to the soil surface. In other cases, no liquid emerged, even after 17 hours following treatment. One hour following treatment, 34 of the 60 bottles contained some effluent (>1 g). At the 17 hour mark, this number had risen to 49. This is shown for each soil condition in Figure 1. For the no-till clay soil, only the columns with measurable effluent at one hour had effluent at 17 hours.

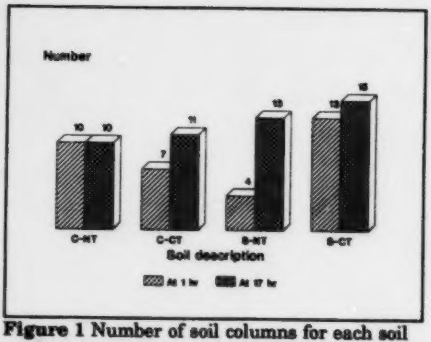

Figure 1 Number of soil columns for each soil condition (out of 15 total) having measurable amounts of effluent at 1 and 17 hours following treatment. (C=clay soils; S=sandy soils; NT=no-till; CT=conventional tillage)

The quantity of effluent (at 17 hours) varied from column to column. There was no significant difference (at $p=0.05$) in the effluent (as percent of applied) between the two soil types or between the two tillage practices (p values were 0.24 and 0.17 resp.). The amount of effluent for the sand with conventional tillage was significantly higher than for clay with conventional tillage and sand with no-till ($p=0.003$).

Figure 2 shows the cumulative totals of effluent for the two soil types and the two volumes of liquid applied. Not surprisingly, the soils receiving three g/cm^2 of liquid had higher volumes of effluent than those receiving only two g/cm^2. Also, for each of the four conditions shown, the greatest effluent yield occurred during the first five hours following treatment.

Bacteria - At the one hour mark following treatment, 20 effluent samples were refrigerated and later analyzed for numbers of fecal coliform, fecal streptoccocus, and *E. coli* bacteria. Subsequent effluent samples were analyzed for only fecal coliform bacteria.

In the first group of 20 samples, levels of the three types of bacteria were similar. The bacteria in the effluent represent 2.6% and 2.2% of the bacteria applied in treatments one and two, respectively - for the 20 soil columns involved. The two tillage methods did not appear to cause any significant differences in the levels of bacteria in the effluent. However, the two soil types were significantly different ($p=0.0002$). The geometric mean of the total number of fecal coliform bacteria for the clay soils (only those soil columns have effluent tested for bacteria) was 41 per cm^2 surface area. This compares to 0.31 for the sandy soils (n=19 and 22, resp.).

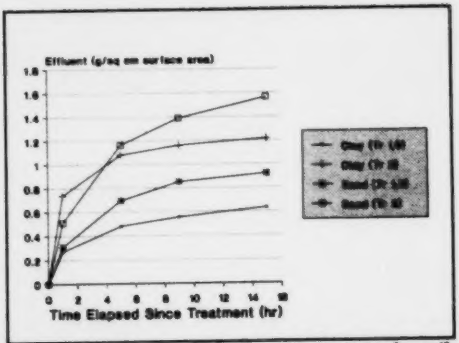

Figure 2 Comparison of effluent quantities by soil type and treatment over time. (Treatment 1,3 equiv. to 2 g/cm^2 applied; Treatment 2 equiv. to 3 g/cm^2)

Chloride - The amount of chloride applied to the soil in Treatment 1 was 4.76 mg/cm^2, and for Treatment 2 was 9.52 mg/cm^2. Unfortunately, the measured levels of chloride in the manure and in the effluent were much lower than expected. Based on the lab results, the Cl application rates were only 0.69 and 1.37 mg/cm^2 for Treatments 1 and 2, respectively. There is no obvious reason for this discrepancy. The chloride levels for the various soil layers (discussed later) were at or about the predicted levels. This suggests that the lab results for the chloride levels in the manure (and therefore, the effluent) were incorrect.

The following can be said about the chloride values that were reported by the lab: a) there were no significant differences in total chloride amounts (expressed as mg/cm^2 of soil surface) between soil types or tillage practices; b) the two manure applications did not produce chloride concentrations in the effluent that were significantly different from the control.

Soil concentrations of chloride told a different story. Figure 3 shows the total amounts of chloride in the soil column for the clay soil. Similar results were found for the sandy soil. In both cases, chloride levels were elevated due to the relative amounts added in the two manure application rates. This elevation of levels was most marked at and near the soil surface, but, in the case of the clay soils, extended right through to the bottom of the soil column. Approximately 40% to 60% of the chloride added to the soil surface (based on the "calculated" concentration of chloride in the manure) was subsequently measured in the soil. The remaining amount of chloride cannot be accounted for. Presumably, some quantity greater than what the lab results suggest was present in the effluent.

Other Parameters - Levels of nitrate-N (NO_3-N) and ammonium-N (NH_4-N) were measured in the manure, soil, and effluent. NH_4-N is considered to be "available" to growing crops. NO_3-N is a soluble form that is leached from the soil relatively easily. These are less stable in the soil than chloride. As a result, the lab results may not

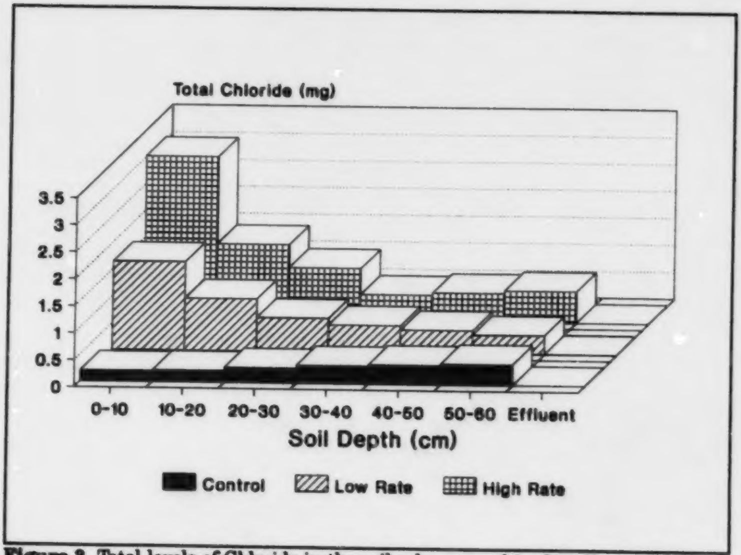

Figure 3 Total levels of Chloride in the soil columns and in the effluent for the clay soils - geom. mean values

provide an accurate representation of the N situation just after manure application. Only 10 to 26% of the $N0_3$-N and NH_4-N applied can be accounted for. The manure application affected the $N0_3$-N and NH_4-N levels to a depth of about 30 cm. The results were similar for the sandy soil, with the NH_4-N levels showing even less pattern.

Soil moisture was measured as the soil was being analysed for chemicals. Ranges in average dry matter content were 73%-82% for the sandy soil and 81%-84% for the clay soil.

Other Observations - The main macropore pathways in the soils in this study appeared to be worm holes. Worm holes were observed in most of the soil columns. These ran vertically and appeared to be continuous to the bottom of the column.

On 8 of the clay columns liquid was ponded on the surface even at 17 hours following liquid application. No effluent emmitted from the bottom of any of these soil columns. It appeared that the surface effectively sealed itself.

CONCLUSIONS

1. The quantity of effluent from the soil columns was not significantly different between the two soil types or between no-till and conventional till. The greatest quantity of effluent was for the sand, conventional tillage.

2. The flow of effluent from the soil appeared to be nearly stopped at 17 hours following treatment, and greater than 50% of the flow occurred during the first 5 hours.

3. At 1 hour following application of liquid to the soil surface, liquid effluent had emitted from 34 of the 60 soil columns.

4. A certain amount of bacteria and chemicals in the manure was detected in the effluent. For the 20 soil columns with the greatest effluent flow at one hour following treatment, just over 2% of fecal coliform bacteria applied was measured in the effluent. The amount of chloride, the tracer chemical, in the effluent was not significantly different for the three treatments (however, problems in the lab analysis of chloride in the liquid samples were suspected).

5. While it appears that some preferential flow (i.e. macropore flow) occurred, it also appeared that raw manure was not flowing intact through the soil column - rather, there was some dilution or displacement taking place.

6. The method of extracting soil columns and testing for macropore flow appeared to work well. The soil columns were the maximum depth possible for the machine and soil conditions encountered.

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AP10

Hydromechanical Behaviour of Fractures at the Clarkson Field Site

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Introduction

The subsurface migration of toxic contaminants from industrial and landfill disposal sites underlain by fractured clay and rock can pose a significant threat to potable water supplies. For fractured rock with low matrix permeability, fractures provide the predominant pathways for subsurface migration of contaminants. A site, near Clarkson Ontario, containing two unconnected horizontal fractures resulting from exfoliation are used in this study. The fractures occur near the surface, at the contact of limestone interbeds within the Meaford-Dundas shale.

Flow in a single fracture is traditionally modelled by assuming the walls of the fractured are parallel and smooth. Because real fracture surfaces are rough and heterogeneous, flow in the fracture plane can be tortuous and deviate from the parallel plate model. In addition, changing stress conditions within the shale, such as excavation of a pit or the emplacement of a berm to contain hazardous wastes, may open or close the fracture thus affecting hydraulic conductivity and solute transport.

In order to study the closure problem, three objectives were defined: 1) to characterize fracture surface roughness and generate stochastic realizations of fracture surfaces, 2) develop a model which describes the closure mechanics of the stochastic surfaces in contact, and 3) to couple deformations resulting from fluid flow in the resulting aperture distribution

Characterizing and Generating Rough Fracture Surfaces

The first step in the analysis of fracture apertures and closure is to obtain core samples from the field containing pre-existing fractures. In the case of this study, fractured clay samples with similar stiffness to the shale at the Clarkson site were obtained. The core is then opened along the fracture plane and profiles are traced using a profilometer.

Following the work of *Brown and Scholz* [*1985*], fractal geometry is employed to characterize and generate fracture surfaces. Using a profile obtained along a direction, x, with N data points, the spectrum is computed by [*Brigham, 1988*];

$$S_x(f_k) = \frac{\Delta}{N-1}\left[\left(\sum_{t=1}^{N} w_t x_t \cos(2\pi f_k t)\right)^2 + \left(\sum_{t=1}^{N} w_t x_t \sin(2\pi f_k t)\right)^2\right] \tag{1}$$

$$f_k = \frac{k}{N},\ k=0,1,2,\ldots\frac{N}{2}$$

where Δ is the data spacing, f_k is the frequency of spectral estimate $S_x(f_k)$ and w_t represents the value of the spatial window function at data point t. Conceptually, the spectrum represents the expected amplitude of asperities (peaks in the surface roughness) with base widths ranging from the length of the profile to twice the discretization interval. When the spectrum is plotted on a $\log\{S_x(f)\}$ vs. $\log(f)$ axes, the fractal dimension D of the profile, which is related to the slope β of the spectrum, is then computed by the relationship [*Voss, 1985a*];

$$D = \frac{(5+\beta)}{2} \tag{2}$$

The fractal dimension of a 1-D profile can be used to generate 2-D fracture surfaces with equivalent roughness by using the method of Random Midpoint Displacement as described by *Fournier* [*1982*] and *Voss* [*1985b*]. Realizations of the fracture surfaces used in this study can be seen in Figure 1.

Hydromechanical Model

To facilitate hydromechanical behaviour, the fracture surfaces are conceptualized as a series of rectangular asperities of different heights (representing surface roughness) resting upon a half space (representing a uniform smooth base). This model is designed to provide information on: 1) the normal stress vs closure of the fracture, 2) the percent contact area during closure, 3) the spatial aperture distribution, 4) nodal fluid pressures, velocities, discharge and 5) fluid deformation effects as a function of the hydraulic gradient and applied pressures.

Closure of the fracture surfaces occurs as the half spaces are pushed together at incremental distance steps of δ. At each closure step δ, displacement continuity is accounted for at each nodal asperity in contact between the two surfaces. A stress/displacement relationship is then solved to yield the nodal force at the contacting asperities since the area of the asperity is assumed constant. The asperities are modelled as 1-D elastic columns for which the stress/displacement equation is given by;

$$\sigma_i = E\frac{\Delta l_i}{l_i} \tag{3}$$

where l_i is the length of asperity i, Δl_i is its change in length, E is the Young's Modulus and σ_i is the stress.

Once the nodal force at a contact point is known, the deformation to the entire half space is calculated creating mechanical interaction between the asperities. The deformation is determined by solving [modified from *Jaeger and Cook, 1976*];

$$w_i = \frac{1-\nu^2}{\pi E}\iint\frac{f_i(\xi,\eta)}{[(x-\xi)^2+(y-\eta)^2]^{1/2}}\,d\xi\,d\eta \tag{4}$$

This integral is solved by mapping the nodal force function and kernel onto a fracture grid consisting of N nodes in the x direction and M nodes in y direction. Each node has some scalar length Δx and Δy and is further subdivided into a subgrid so that nodal force is mapped as a step function as opposed to a point load. The 2-D discrete Fourier transform of both the force and kernel functions are then computed and multiplied together to form a circular convolution. The 2-D inverse Fourier transform is then applied to calculate nodal displacements w_i.

Fluid flow in the aperture distribution is found by solving the Navier-Stokes equation for uniform flow between parallel plates. Assuming flow is incompressible, viscosity and density are constant, and the viscosity term dominates, nodal discharge is calculated by [*Bear, 1972*];

$$Q_i = \frac{\rho g}{12\mu}(2b_i)^3\nabla h \tag{5}$$

where Q_i is the discharge at node i, ρg is the unit weight of the fluid, μ is the viscosity, 2b is the nodal aperture and ∇h is the hydraulic gradient. Hydraulic head, h, is related to pressure P by dividing by the unit weight of the fluid and adding a datum elevation. Assuming fluid flux conservation such that;

$$\nabla\cdot Q_i = 0 \tag{6}$$

nodal hydraulic heads are found by writing (6) in finite volume form and assembling the global matrix with constant head boundaries at opposite ends of the fracture and zero flux boundaries applied to the remaining two sides. Nodal heads are then converted to pressures to determine fluid deformation effects.

Hydromechanical behaviour of the fracture surfaces is achieved by relating the nodal pressures caused by fluid flow to the nodal forces causing deformation of the asperities and the half spaces. Because the asperities and half spaces deform linear elastically, all strain results during closure become dimensionless when divided by the Young's Modulus. Stress results with hydromechanical behaviour are made dimensionless by dividing the pressure at the inflow boundary by the Young's Modulus for a given pressure gradient.

Results and Discussion

Surfaces were generated for this study using a fractal dimension of D = 2.135 with a standard deviation of σ = 0.7613mm based upon measurements obtained from clay fracture profiles. Surfaces were modelled using 64 by 64 nodes with each node having an 8 by 8 node subgrid. The dimensions of each node were 0.001m in the x and y directions. This particular geometry was employed due to instability in the closure algorithm when the width of the asperities becomes much greater than the mean height. In addition, the stress results during closure can be made dimensionless by dividing by the Young's Modulus. If the width of the nodes become too large, the problem may be stable but the results may not be dimensionless. The node dimensions chosen were the optimum for stability and dimensionality.

Stress vs strain curves are constructed for closure of surfaces exhibiting hydromechanical behaviour. Curves showing total contact stress, σ, for various fluid pressures, P, at the inflow boundary were made dimensionless by dividing by the Young's Modulus E (Figure 2). Closure of the half spaces is divided by the maximum aperture of the undeformed aperture distribution. A strain of 1.0 thus represents maximum closure.

Hydromechanical behaviour with dimensionless pressure at the inflow boundary, P/E, equal to 0.0001 is indistinguishable from P/E equal to 0.0 (no hydromechanical behaviour). When P/E equals 0.001, stress-strain results are significantly different. This is due to nodal fluid pressures which cause asperities which were not in contact to push into the half spaces of the upper and lower fracture resulting in the separation of some neighbouring asperities which were in contact, thus reducing contact stresses. This effect is particularly evident for P/E equal to 0.01. In this case, none of the asperities contacted until a strain of approximately 0.2 was attained.

Discharge though the fracture computed by solving for flow in the aperture distribution agrees very well with flow computed by taking the arithmetic mean of the aperture distribution and using the parallel plate model (Figure 3). This is surprising given the tortuosity and channelling as seen by the nodal fluid velocity vectors (Figure 4) in the aperture distributions with 0, 10 and 20% contact area (Figure 1).

Conclusions

Numerical simulations conducted for this study indicate that the deformation characteristics of a fracture can be significantly influenced by the presence and migration of a fluid. Discharge in the deformed aperture distributions appears to agree well with the parallel plate model despite significant tortuosity in the flow path.

Future development will include the derivation of constitutive relationships involving stress, strain, flow and contaminant transport within fractures using a Monte-Carlo simulation approach. These relationships will be built into a realistic 3-D model representing the fracture network at the Clarkson Field site.

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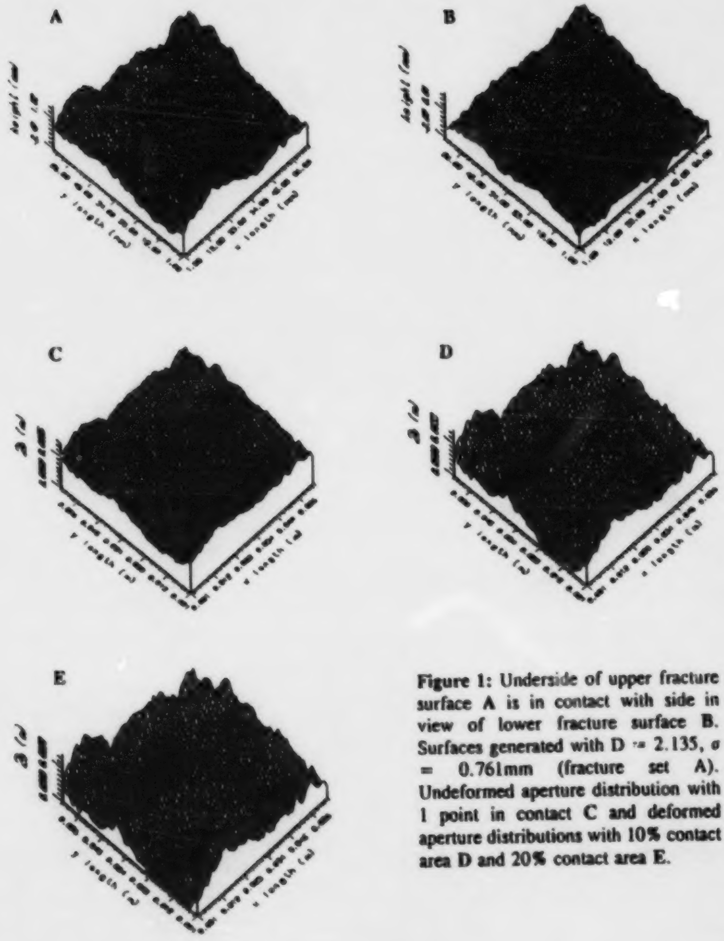

Figure 1: Underside of upper fracture surface A is in contact with side in view of lower fracture surface B. Surfaces generated with D = 2.135, σ = 0.761mm (fracture set A). Undeformed aperture distribution with 1 point in contact C and deformed aperture distributions with 10% contact area D and 20% contact area E.

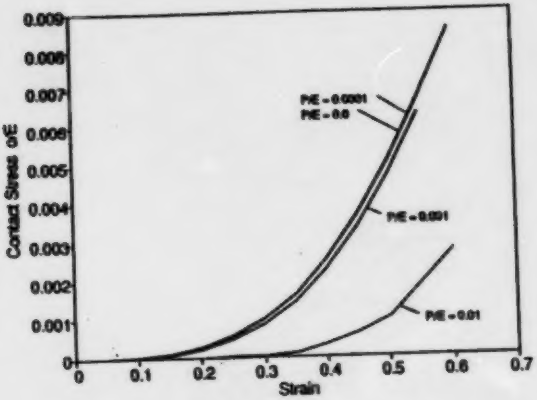

Figure 2: Total contact stress at points of contact vs strain for various different dimensionless fluid pressures (P/E) at the inflow boundary

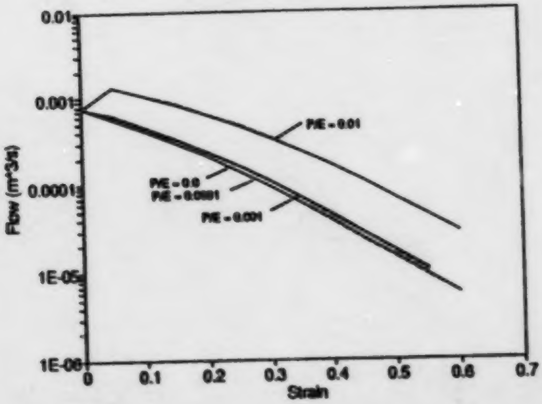

Figure 3: Flow vs strain with hydromechanical behaviour. Solid lines are flow in aperture distribution, dashed lines are flow using cubic law and arithmetic mean aperture.

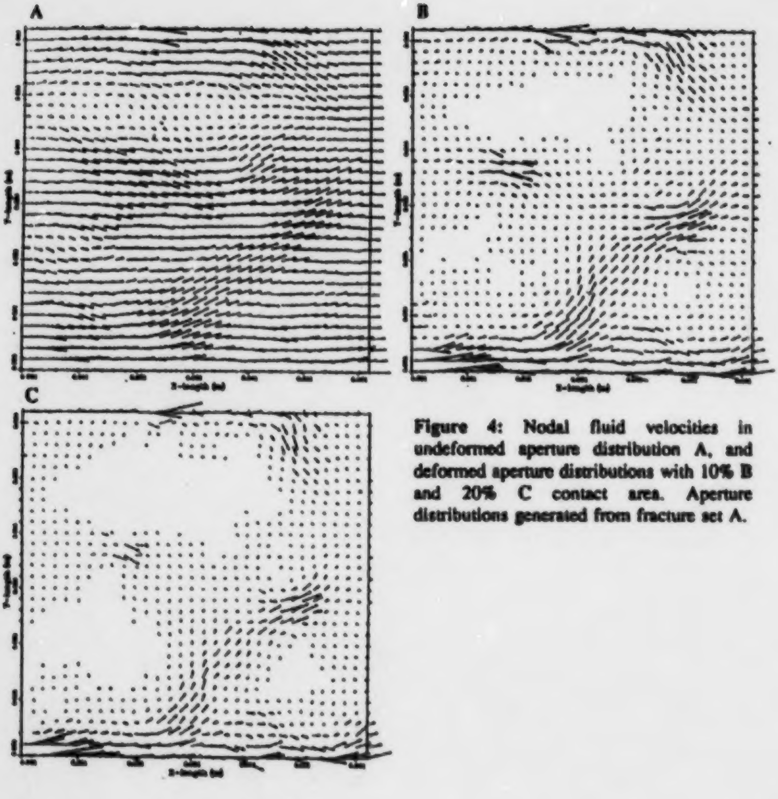

Figure 4: Nodal fluid velocities in undeformed aperture distribution A, and deformed aperture distributions with 10% B and 20% C contact area. Aperture distributions generated from fracture set A.

Abiotic factors involved in predicting trace metal levels in freshwater bivalves.

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INTRODUCTION

Trace metals are progressively added to the aquatic sediments where they pose a potential threat to benthic organisms. The development of rational effective and economical strategies to solve the problem of contaminated sediments will depend greatly on our ability to predict how remedial actions will improve water quality and how the changed conditions will affect aquatic organisms. A promising approach to the prediction of metal bioaccumulation by benthic organisms, and eventually to the prediction of metal effects on this community, would be to develop deterministic models based on sound geochemical and biological principles. The present study represents an attempt to develop such a deterministic model of general applicability to predict the bioaccumulation of cadmium by the freshwater bivalve *Anodonta grandis*. In the formulation of the model, we use concepts derived from the free-ion activity theory of metal-organism interactions, and from surface complexation theory, to relate Cd concentrations in the bivalve to those in the water or in the surficial sediments.

METHODS

Oxic surficial sediments (top first 0.5 cm), associated overlying water samples (obtained with porewater peepers) and bivalve specimens, when present, were collected within a study area of 350 000 km^2 at 50 littoral stations located in 38 lakes. Water samples were analysed for Cd, pH and major ions. Sediment samples were extracted with various reagents, analysed for Cd, Fe and organic carbon concentrations. The soft parts of the bivalves were pooled (10 organisms) and analysed for Cd.

RESULTS AND DISCUSSION

According to surface complexation theory, the adsorption of a trace metal, M, on iron oxyhydroxide surfaces can be expressed in a simplified manner (Benjamin and Leckie, 1981) by:

$$\equiv Fe-OH_x \;+\; M^{z+} \;\overset{*K_{Fe}}{=}\; \equiv Fe-OM \;+\; x\,H^+ \qquad (1)$$

$$*K_{Fe} = \frac{\{\equiv Fe-OM\}\,[H^+]^x}{\{\equiv Fe-OH_x\}\,[M^{z+}]} \qquad (2)$$

where charges on the solid species are omitted for simplicity; $*K_{Fe}$ is an apparent overall equilibrium constant and "≡", {} and [] refer to adsorption sites, and concentrations of solid and dissolved species respectively. Assuming a low surface coverage by M, and relating the concentration of free sites to that of iron oxyhydroxides (i.e. $\{\equiv FeOH_x\} = N_{Fe}\ \{Fe\text{-}oxide\}$, and the concentration of occupied sites to that of M associated with Fe oxyhydroxides (i.e. $\{\equiv FeOM\} = \{Fe\text{-}OM\}$) leads to (Tessier, 1991):

$$^{*}K_{Fe} = \frac{\{Fe\text{-}OM\}\ [H^{+}]^{x}}{N_{Fe}\ \{Fe\text{-}oxide\}\ [M^{z+}]} \tag{3}$$

Laboratory bioassays, conducted with marine benthic animals exposed to dissolved metals under carefully controlled conditions have shown that the effects of trace metals on these animals are related to the free metal ion concentrations and not to the total metal concentrations. For example, mortality of the shrimp *Palaemonetes pugio* exposed to cadmium was shown to be proportional to $[Cd^{2+}]$ (Sunda *et al.*, 1978). Similarly, short-term accumulation of copper in the American oyster *Crassostrea virginica* was found to be proportional to $[Cu^{2+}]$ (Zamuda and Sunda, 1982). These observations are manifestations of the free-ion activity model (Morel, 1983); for bioaccumulation of a trace metal in an organism, it can be written:

$$[M(org)] = K_p\ [M^{z+}] \tag{4}$$

where $[M(org)]$ is the trace metal concentration in the organism, and K_p is a proportionality constant. Combining equations (3) and (4) leads to:

$$[M(org)] = \frac{K_p}{N_{Fe}\ ^{*}K_{Fe}}\ \frac{\{Fe\text{-}OM\}\ [H^{+}]^{x}}{\{Fe\text{-}oxide\}} \tag{5}$$

In equation (5), K_p, N_{Fe} and $^{*}K_{Fe}$ are constants, and the quotient comprising $\{Fe\text{-}OM\}$, $[H^{+}]^{x}$ and $\{Fe\text{-}oxide\}$ can be considered as a surrogate measure of $[M^{z+}]$. The use of equation (5) is illustrated by taking as an example the *in situ* accumulation of Cd, a non-essential trace metal, in the freshwater pelecypod *Anodonta grandis* (Figure 1c). The values of $\{Fe\text{-}oxide\}$ (mole Fe g^{-1}) is estimated from the iron concentration extracted from the oxic sediments with a reducing reagent ($NH_2OH \cdot HCl$); sedimentary Cd extracted with $NH_2OH.HCl$ is taken as an estimate of $\{Fe\text{-}OCd\}$. The success of the surrogate measure in explaining the accumulation of Cd in the freshwater bivalve *Anodonta grandis* can be appreciated by comparing in Figure 1 c with a and b where other predictors of $[Cd(org)]$ are used. Several comments are formulated below concerning Figure 1.

When Cd concentrations in the bivalves are compared with total cadmium concentrations in the sediments, no relationship emerge (Figure 1a). Past attempts to relate total metal concentrations in surficial sediments to metal levels in indigenous organisms have generally proven disapointing; Figure 1a offers another example of the failure of this approach. Even when apparently successful within a limited geographical area, such empirical models cannot be used to extrapolate beyond the original data used to develop the statistical relationship.

Similar conclusions (i.e. no significant relationship) are reached if the predictor considered is the ratio Cd/Fe extracted with $NH_2OH.HCl$ (Figure 1b). Such an empirical normalization by iron oxyhydroxides as in this case or by organic carbon has been advocated for the prediction of As, Cu, Hg and Pb bioaccumulation in bivalves (Langston 1980, 1982; Luoma and Bryan, 1978; Tessier *et al.*, 1983, 1984). The present study offers a likely explanation for these findings. The

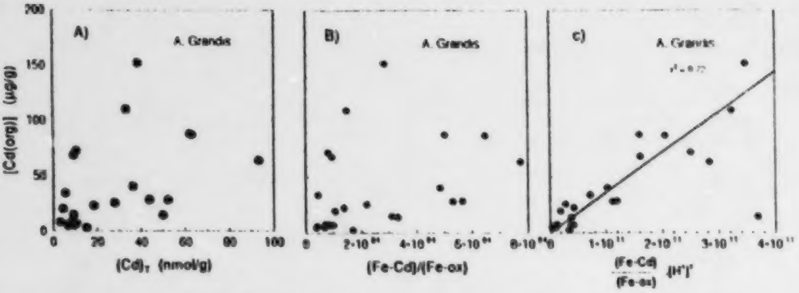

Figure 1. Relationship between Cd concentration in the soft tissues of *A. grandis* and total sedimentary Cd ($\{Cd\}_T$; A), ratio of Cd and Fe extracted with $NH_2OH.HCl$ ($\{Fe\text{-}Cd\}/\{Fe\text{-}oxide\}$; B) and the same ratio multiplied by $[H^+]^x$ (C).

studies of Langston (1980, 1982) and Luoma and Bryan (1978) were performed in estuaries, where the pH is relatively constant; the freshwater studies (Tessier *et al.*, 1983, 1984) were carried out in three lakes located in a restricted geographical area where the lake pH is relatively constant. In such case, $[H^+]^x$ becomes approximately constant in equation (5) and sedimentary Cd normalised with respect to iron oxyhydroxides (or organic carbon) becomes a good predictor of [M(org)]; a logical consequence is that these predictors are not "universal" in the sense that their application should be site dependent (i.e. restricted to a narrow pH range).

The right-hand quotient in equation (5) is a relatively good predictor of cadmium concentration in *A. grandis* (Figure 1c) except for one outlier (Harp Lake). Improvement to the prediction is expected when a better estimator of {Fe-OM} will be used. Indeed, there are some indications in the literature that organic matter can compete with iron oxyhydroxides in oxic sediments to sorb Cd (Lion *et al.*, 1982). The use of sedimentary Cd extracted with $NH_2OH.HCl$ may overestimate {Fe-Cd}; this effect would be amplified for lakes at low pH. Sediment in Harp Lake (pH 6.93) present relatively large ratio {organic carbon/Fe oxyhydroxides} compared to other low pH lakes.

Refinement of the proposed model, or the formulation of better ones, will require a better understanding of the geochemical and biological processes involved in the bioaccumulation of trace metals by benthic organisms. For example, the nature of the sorption reactions that are responsible for the presence of trace metals in oxic sediments is still poorly understood. Similarly, improved knowledge of the feeding strategies of benthic animals would aid in the development of any future models.

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The 1990 Toronto Personal Exposure Pilot (PEP) Study

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INTRODUCTION

In a recent City of Toronto Department of Public Health survey, air pollution and its associated problems were identified by the majority of respondents as being their major environmental concern in the Toronto area. As a result of the City's initiative to analyze urban air for gaseous compounds not routinely monitored by themselves and other agencies, and the Ministry's mandate to investigate atmospheric concentration levels of volatile organic compounds (VOCs) to which people are exposed, the need to establish a current air toxic VOC data base characterizing the major microenvironments in which people work and live was realized. During the summer of 1990, the Air Resources Branch (ARB) undertook an air quality personal exposure pilot (PEP) study in order to characterize the indoor (home and office), outdoor (downtown and residential) and commuting microenvironments. In 1988, W.R. Ott[1] reported that from time budget analyses of employed people in 44 different U.S. cities, only 2% of their time was spent outdoors whereas 6% was spent in-transit, 28% indoors at work and 63% indoors at home. In Toronto, it is estimated that people spend less than 10% of the time outdoors.

METHODOLOGY

Following an 8-day, mid-week cycle, 65 field samples were collected between June 11 and August 29. Samples were obtained by drawing 12 to 24 litres of air through three-stage adsorbent cartridges and each sample was analyzed by Gas Chromatography using Flame Ionization and Mass Selective Detectors (GC/FID/MSD). Samples were thermally desorbed and focused onto the head of a triple GC capillary column system (two DB-1 phase and one DB-5 phase), and eluted into two FIDs and the MSD. Identification was based on relative retention times and mass spectral signatures, while quantification employed FID responses. Although each sample was scanned in the range of C_5 to C_{13}, no significant amounts of any unknown compounds were detected. In order to facilitate quality control, quality assurance and interpretation, the number of target compounds was reduced to 22 of the more ubiquitous aliphatic and aromatic volatile organics and their haloginated analogues as shown in Table 1.

The four microenvironments studied were:
Outdoor. Sixteen outdoor samples were obtained in the "downtown office" and 7 samples were obtained in the "downtown residential" areas of Toronto. All samples were taken over 12-hour periods at a height of 1.5 metres above ground.
Indoor: Office. Eight samples were obtained in several unoccupied offices and one laboratory in downtown Toronto. Sampling was carried out during the regular work day in a "smoke-free workplace".
Indoor: Home. Four samples were obtained at different residences within the Toronto airshed; namely, Oshawa, Thornhill, Scarborough and Richmond Hill. The sampling was conducted overnight with durations up to 16 hours.
Commuting. In order to simulate the typical commuter's exposure to VOCs, several ARB staff members collected air samples while enroute to and from their residences and work, and as they walked about during their noon hours in downtown Toronto. All were non-smokers who refrained from wearing any type of perfumes or lotions. The air samples were collected by personal sampler units and the sampling was conducted within the inhalation zone of each participant. The samples were of 1 to 2-hours in duration and 11, 8 and 8 samples were collected during the morning, noon and afternoon periods respectively.

RESULTS AND DISCUSSION

The Outdoor Environments: Downtown and Residential

With respect to the ambient VOC data, the overall average concentrations were very low and similar to the results obtained by others (R. Bell[2], T. Dann[3] and J.J. Shah[4]). Average VOC concentrations were less than 20 $\mu g/m^3$ and usually, only 20 to 25 different VOCs were detected in each sample. Samples acquired at the 2 locations had similar chromatographic profiles. The dominant VOCs were the low-boiling alkanes, aromatics (benzene, toluene and xylenes) with trace amounts of chlorinated and substituted benzenes. From a diurnal perspective, the ambient nighttime VOC concentrations measured at the downtown site were slightly higher than those measured at the residential site (Figure 1). This slight increase was thought to have resulted from the poorer atmospheric dispersion conditions and larger traffic volume in the downtown area.

The Indoor Environments: Office and Home

No unusual odours were detected in the offices or homes and all VOC concentration levels were less than 85 $\mu g/m^3$. The chromatographic signatures of both the office and home samples were similar. Low-boiling alkanes, aliphatics, aromatics and some chlorinated aliphatics predominated, but some higher-boilers were also detected. Major sources of indoor aliphatics and aromatics are floor waxes, wood stains, furniture polishes, room fresheners and adhesives. B.A. Tichenor[5] suggested that outgassing of chlorinated water was a major source of trichloroethene and other chlorinated organics and that drycleaning was a major source of tetrachloroethene. Higher ordered VOCs are attributed to cleansers, detergents and household solvents.

Outdoor Versus Indoor Air Quality

As noted in Figure 2, the indoor air quality data was highly variable and upon examining the 22 more ubiquitous compounds, some indoor concentrations were as much as 2 to 5 times higher than the outdoor air concentration levels. This observation is also supported by other researchers in this field; for example, B.A. Tichenor[5] and H. Greim[6]. Because of this apparent and significant increase in concentration levels indoors and the assumption that people in the Toronto area may only spend 10% of their time outdoors, one must ask if enough emphasis is being placed on indoor air quality studies compared with the current ambient (outdoor) air monitoring programs.

Commuting

Five ARB staff members using some combination of car and public transit (subway or train), participated in this phase of the PEP study. The interpretation of the acquired data suggests that as the percentage use of the car increased, so did the concentration of VOCs found in the sample. As noted in Figure 3, the morning rush-hour samples appeared to have higher VOC concentrations than those collected during the afternoon rush-hour. This may be explained by the longer rush hour periods and the better atmospheric dispersion conditions usually present in the afternoons as noted in similar work by C.C. Chan[7]. Staff members also collected one-hour samples while walking in downtown Toronto. However much lower concentrations and only 20 to 25 different VOCs were detected in these samples.

It was interesting to note that based on 45 of the more prevalent VOCs measured during this study, the total VOC concentrations differed in each microenvironment, but the relative concentrations of the aliphatics, aromatics and chlorinated VOCs were similar (Figure 4).

CONCLUSION

The PEP study represented an initial step to investigate the exposure of individuals in the Toronto area to various VOCs. The acquired VOC data set is limited and therefore the conclusions, comparisons and observations are tentative and conservative. Generally, all measured VOC concentrations were low (none of the applicable Ministry Air Quality Standards, Criteria or Guidelines were exceeded) and no unusual odours were detected during any of the sampling periods. Since people working and living in Toronto usually spend only 10% of their time outdoors, air quality from a personal perspective must be explored in greater detail if comprehensive human exposure assessments are to be carried out.

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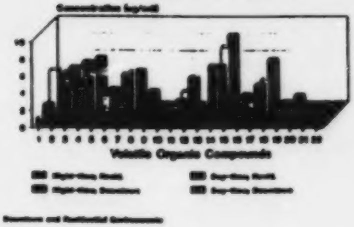
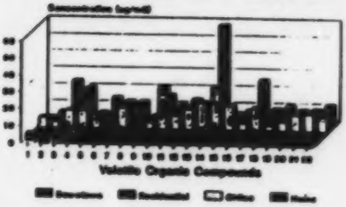
Major VOCs of the PEP Study
Table 1 (Toronto 1990)

1	PROPANE
2	CHLOROMETHANE
3	BUTANE
4	PENTANE
5	1,1-DICHLOROETHENE
6	DICHLOROMETHANE
7	HEXANE
8	TRICHLOROMETHANE
9	1,2-DICHLOROETHANE
10	1,1,1-TRICHLOROETHANE
11	BENZENE
12	TETRACHLOROMETHANE
13	TRICHLOROETHENE
14	TOLUENE
15	TETRACHLOROETHENE
16	ETHYLBENZENE
17	XYLENES
18	STYRENE
19	NONANE
20	1,3,5-TRIMETHYLBENZENE
21	DECANE
22	1,2-DICHLOROBENZENE

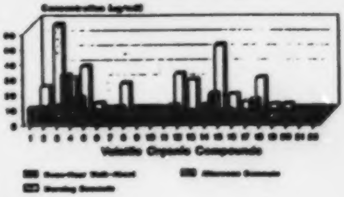
1990 PEPS VOC Results
Diurnal Variations (Figure 1)



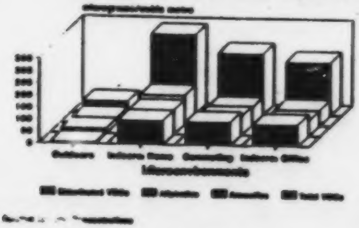
Personal Exposure Pilot Study
Outdoor Versus Indoor (Figure 2)



Personal Exposure Pilot Study
Commuting (Figure 3)



1990 Toronto Pep Study
Volatile Organic Compounds (Figure 4)



AP13

MODELLING and METEOROLOGICAL RESPONSE TO ENVIRONMENTAL EMERGENCIES

by
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1. INTRODUCTION: The ever increasing demand for chemicals, their manufacturing, transportation , storage and use has posed a serious environmental problem. Inspite of extensive precautions , accidental releases of chemicals occur occasionally during all four phases of chemical use. In some cases, such as Bhopal(India) and Mexico City(Mexico), an accidental chemical release can have devastating effects.

In addition to environmental problems posed by chemical spills, generation of electricity by nuclear energy poses its own problems. The nuclear energy industry has very stringent controls in all phases of its operation , however inspite of these controls accidents can occur (e.g. Chernobyl and Three Mile Island). In Ontario there are three nuclear energy generating stations. To deal with any emergencies at these locations Emergency Planning Ontario of the Ministry of Solicitor General has devised a nuclear emergency plan and is the principal coordinator for emergency preparedness in Ontario. Environment Canada, Ontario Ministry of Environment, Atomic Energy Control Board, Atomic Energy of Canada Ltd., Ontario Hydro and the municipalities in which the nuclear reactors are located form the group overseeing any nuclear emergency.

There have been several environmental emergencies in Ontario involving chemicals where evacuation of large populations has been deemed a prudent precaution. In order to deal with such events, Air Resources Branch as part of the Ministry of Environment's (MOE) spills action response, developed an EMERGENCY RESPONSE PROGRAM. There are two aspects of the program, MONITORING and MODELLING/METEOROLOGY. This paper concentrates on the MODELLING and METEOROLOGY part of the program.

2. EMERGENCY RESPONSE PROTOCOL: In order to minimise environmental impact and human exposure in case of a chemical accident, it is important that appropriate mitigation measures are taken immediately. As a part of their mandate the Ministry of the Environment passed a SPILLS Bill. A Spills Action Centre was established to coordinate the response of the Ministry. This centre is manned 24 hrs a day and under the spills act all chemical spills are to be reported to this centre. The centre then contacts the appropriate MOE's regional branch to mobilise MOE personnel. In many instances some form of mathematical modelling and/ or meteorology is required to determine the area of impact and ground level concentrations. The modelling group of Air Quality and Meteorology Section of the Air Resources Branch provides this information. A staff of six forms part of the response team of ARB. Members of this team are on a two week rotating roster and are on call 24 hrs a day. The person on call has at home during their two week assignment, a state of the art portable PC with mathematical models required for determining air concentrations. MOE staff at the spill site provides necessary input data required by the model.

The modeller/meteorologist on duty computes ground level concentrations and passes this along with any pertinent information on future meteorological conditions back to MOE personnel at the site. These data along with TLV,STEL and IDLH(threshold limit value, short term exposure level and immediate danger to life and health) data for the chemical of concern are then used by the response team on site in determining their actions such as safe areas and evacuation zones.

The models implemented on the portable PC provide first cut conservative estimates of ground level concentrations which are essential in providing a quick response to the emergency on hand. After the emergency is over or if it is of a long term nature (e.g. train derailment in Mississauga in 1979, with subsequent chlorine leak), more comprehensive models are available to determine with greater accuracy the impact of the spill. The reliability of input information such as the amount of chemical released often limits the accuracy of predicted concentrations.

3. MODEL DESCRIPTION: The Emergency Response Program is a multi module program written in BASIC. BASIC language was chosen for its simplicity and ease of screen manipulation. The program is driven by menus and is very user friendly. Default values of the variables are provided if field data are not available. A flow chart of the program is shown in Fig. 1. Each module is described briefly in the following sections.

METEOROLOGICAL MODULE:

Dispersion of any pollutant released into the atmosphere is strongly governed by the prevailing meteorological conditions. Dispersion is limited if the winds are weak and/or if there is a low level inversion layer limiting vertical mixing. Three types of inputs are entered through this module:

METEOROLOGICAL : Prevailing meteorological conditions such as

- -Wind Speed/Direction
- -Temperature
- -Cloud cover
- -Precipitation (snow/rain)
- -Mixing layer depth (default used if not available)

SITE INFORMATION : -Surface roughness (i.e. forests, cultivated fields, urban area etc.)

RECEPTOR LOCATION : -Downwind and crosswind (location of points of concern)

SOURCE INFORMATION: -Emission rate (if known)

-If emissions from stack then stack parameters

-Dimensions of building if present

-If the incident involves a fire or explosion an onsite estimation of the plume/puff rise

The program then computes all parameters needed to perform dispersion calculations. The computed data are then written to a file which is accessed by other modules in the program.

CHEMICAL INFORMATION :

In addition to meteorological information, chemical properties of the emissions are required. A simple database containing physical properties as well as Threshold Limit VALUE (TLV), Short term Exposure Limit (STEL) and Immediate Danger to Life and Health (IDLH) values where available for about 400 chemicals forms part of the program. If a chemical is not listed in the database but its properties are known, they can be entered into the database easily. When the desired chemical is located in the database, the program extracts the required data and writes to a file which is then used by other programs. The use of files for transferring the data from module to module ensures that if a rerun is required with say one parameter changed, then only the new variable needs to be entered, the remaining data is readily available from the old data files.

SOURCE CALCULATIONS :

If the accident involves a container such as a tank (which is generally the case) and the entire contents are not spilled, this program then computes the expected rate of emission from the container. If the contents are spilled on to ground and form a liquid pool, the program then computes the evaporation rate from the pool. The size of the pool would be obtained from onsite MOE personnel. Emission rates for continuous or instantaneous releases are computed and written to a file for use by other modules.

SIMPLE - GAS DISPERSION MODEL

This model is a simplified mathematical description of the mixing (in ambient air) of the released gas as the material moves downwind. It is conservatively assumed that the material is released at ground level. As the pollutant travels downwind, it mixes both horizontally and vertically with ambient air thus reducing concentrations within the plume or puff.This module can handle both instantaneous and continuous releases. Figs. 2 and 3 show the development of a plume and a puff in the simple gas model.

HEAVY GAS MODEL

The behaviour of a gas which is denser than air is very different than that of a gas lighter or same density as that of the air. If the released gas is denser than air (at least 1.25 > than air), the cloud slumps to ground due to gravity. Similarly if the release is from a stack the plume sinks instead of rising as in the case of positive buoyancy.

When an instantaneous release of a heavier than air gas occurs it forms a cloud. The model assumes that this cloud is cylindrical in shape with a radius 'R' and height 'H'. Due to gravity effects, the cloud slumps. In order to keep the model simple, it is assumed that during slumping it does not entrain air. When the gravitational forces are balanced by the frictional forces the slumping phase is assumed to be complete. The slumped cloud then entrains air at the top surface and starts to grow. As is the case in the simple gas model, a maximum height equivalent to the mixing layer depth is imposed on the cloud by the model. The cloud is advected downwind with the wind speed computed at the clouds average height at any given time.

At present only an instantaneous release of a heavy gas is handled by the model.

The model outputs concentrations in the cloud, cloud radius and height and the location of leading and trailing edge of the cloud. This output can be stored for plotting or directed to a printer as desired. Fig. 4 shows a schematic of the dispersing heavy gas puff.

GAS MODEL (Module from Proposed CAP MODELS)

This model was developed for regulatory purposes. It is a comprehensive plume model which can deal with all atmospheric stabilities and various release characteristics in a realistic manner. Ground level releases as well as elevated buoyant or neutral releases can be handled. Receptor locations can be defined on a grid or at any arbitrary locations. Buoyancy flux can be input if the accident involves a fire or an explosion and the resulting plume is buoyant. The model output can be either directed to screen or to a file for processing.

ERP MODEL EXECUTION

As shown in Fig. 1, the main entry is through METINFO. Current or past meteorological , source and receptor information is entered in this module. This information remains unchanged until new information is entered. Control is then passed on to the GAS subprogram which allows the user to select one of the models described in section 3. Prior to execution of the model , the user can select the desired chemical from the database. This information is also stored until changed in subsequent runs. After computing concentrations, control is passed back to the main menu. Different scenarios can be run by only changing the desired parameters.

Run time greatly depends upon the number of receptor points. On a standard PC equipped with a math coprocessor, the heavy gas module takes about 60 seconds to complete one run for about 100 receptors. The other models execute more quickly. Run time is longer (about one and a half times) if there is no math coprocessor.

PICKERING/BRUCE/DARLINGTON ERP

There is a separate emergency response program for nuclear generating stations. Each site has a different reactor design necessitating separate programs for source calculations. However, once the source term is determined, the atmospheric dispersion model is similar for all sites. The model was developed for surface releases. However low level elevated releases can be handled by the model under certain conditions (e.g. when the plume from an elevated release mixes quickly in the mixed layer). Meterological data, current or forecast (up to 24 hrs) are input to the model. The computed ground level concentrations are then used by a dose calculation module which computes the uptake of various radioactive species by humans. Based on these dose levels different protective actions such as use of iodine pills, sheltering or evacuation are taken.

In order to provide a meteorological forecast of local winds MOE developed a three dimensional wind field model which can resolve local winds such as a lake/land breeze. This model is intended to assist the forecaster in incorporating local effects into his wind forecast.

REAL TIME USE OF ERP

AOM has used the chemical ERP modelling package for a number of years in real emergencies. On the average the response time from the initial call has been around one hour. Most of the time is spent obtaining adequate information about the accident, from the site. The accidents covered ranged from explosion in chemical storage areas, releases from stacks, liquid spills from chemical processing areas, tire fires and train derailments. Some examples of recent cases where dispersion modelling was required during or shortly after an accidental release are : Hagersville Tire Fire, Tetraethyl Lead release in Sarnia, a fire in chemical storage room in Etobicoke, a small tire fire near Niagra Falls, an HCL spill in Stoney Creek and a train derailment near london involving a spill of Chloro-sulphonic acid. Although the algorithms used in these models are relatively simple (except the GAS model), the information provided to the field staff at the site of a chemical spill has proved to be valuable.

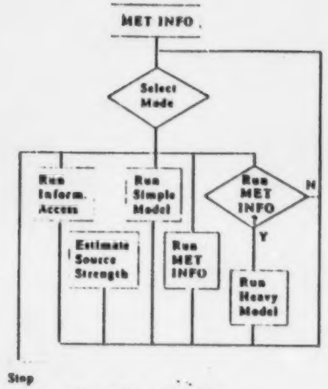
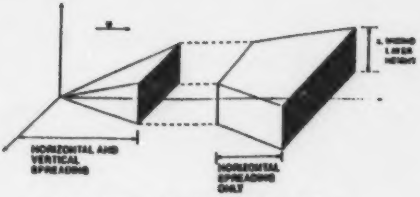

MET INFO
Select Mode
Run Inform. Access
Run Simple Model
Run MET INFO
N
Y
Estimate Source Strength
Run MET INFO
Run Heavy Model
Stop

Fig 1. Flow Chart For Emergency Response Program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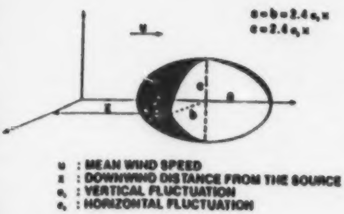
MIXING LAYER HEIGHT
HORIZONTAL AND VERTICAL SPREADING
HORIZONTAL SPREADING ONLY

Fig. 2: Dispersion from a Ground Level Source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$a=b=2.4\sigma_y x$
$c=2.4\sigma_z x$
c
a
b
x
u : MEAN WIND SPEED
x : DOWNWIND DISTANCE FROM THE SOURCE
σ_z : VERTICAL FLUCTUATION
σ_y : HORIZONTAL FLUCTUATION

Fig. 3: Dispersion of a Puff

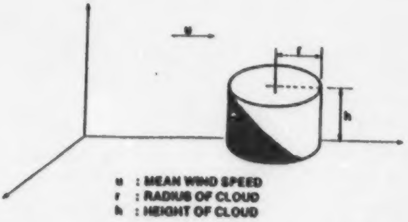
u
r
h
u : MEAN WIND SPEED
r : RADIUS OF CLOUD
h : HEIGHT OF CLOUD

Fig. 4: Dispersion of a Heavy Gas Cloud

AP14

Analysis of Persistent Ozone Episodes in Southern Ontario 1980-1991.

by

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Introduction

It has been established that widespread air pollution episodes, over southern Ontario due to ozone, can occur each year during the months of May to September. Ozone episode-days are defined as days on which widespread (hundred of kilometres) elevated ozone levels (greater than 80 ppb maximum hourly concentration) occur at eight or more monitoring sites in southern Ontario and episodes are defined as distinct events associated with episode days. These episodes arise mainly from an influx of ozone and its precursors (oxides of nitrogen, NO_x, and volatile organic compounds, VOC) from the industrial states south of the lower Great Lakes, and are generally associated with slow moving high pressure systems characterized by meteorological conditions which are conducive to photochemical production of ozone i.e. warm temperatures, relatively clear skies and low wind speeds. Yap et al. (1988) indicated that widespread episodes tend to occur under weather classes generally indicative of back or center of high pressure situations (Fig.1).

During the twelve year period 1980 to 1991 there were eight ozone episodes, over southern Ontario, which had durations of four or more days (Table 1). The longest episode lasted eight days and occurred during the period June 10-17, 1983. The episode of July 4-10, 1988 was identified as the worst episode experienced. It should be noted that four of the eight episodes occurred during the summer of 1988, the hottest summer during the last decade.

It has been shown by Pagnotti (1990) that in the New York metropolitan region, ozone episodes lasting three or more consecutive days are correlated with 850 mb temperatures of 18 C and greater, thus in this paper the synoptic weather patterns associated with episodes are reviewed and meteorological data, particularly air temperature and relative humidity at various levels of the atmosphere, are examined to determine their relationships to elevated surface ozone levels.

Data and Analysis

Upper air data from the nearest radiosonde stations (Flint, Michigan and Buffalo, New York) in the vicinity of southern Ontario were retrieved, for all the episodes, from the archives of the Ministry of Ontario's Meteorological Data Acquisition System (MDAS). The vertical structures of the high pressure systems during the episodes were examined. These warm core high pressure systems intensify with height and as a result cyclones (unstable weather systems) are prevented from travelling directly eastward. Surface meteorological data were also analysed along with air parcel back trajectories and residence times which were computed using a modified version of the trajectory model developed by Yap and Kurtz (1986). The model was modified to incorporate meteorological conditions such as speed of the air mass, average surface temperature and cloud cover along the path of the air parcel, using surface observations closest to the path of the trajectory. Ozone data were obtained from the Ministry's Air Quality Information System (AQUIS) data base. Examples from various episodes are used to examine how meteorology plays a very important role in the development of the ozone episodes.

Results And Discussion

An examination of the eight episodes which occurred over southern Ontario during the past twelve years, indicates that they were all associated with stagnant or slow moving high pressure systems centered south of the lower Great Lakes, with a blocking flow pattern aloft. An illustration of the relationship between the surface and 500 mb flow patterns is given in Fig. 2. A strong vertical coupling between these levels occurs. Under this type of synoptic situation, a deep, stagnant, warm high pressure system develops and results in a deep layer of subsidence and light winds. Due to large scale subsidence, convective activity is reduced, the stability of the boundary layer and the dew point depression increase Fig. 3. The resultant clear skies and dry conditions are thus conducive to increased photochemical activity of the lower atmosphere. Table 2 shows the dry bulb and dew point temperatures at the 850 and 700 mb levels at Flint, Michigan, at 2000 EDT during the period July 3 to 10, 1988. Note that at the 850 mb level, the dry bulb temperatures ranged from 13 C to 21.8 C and the dew point temperatures ranged from 0.8 to 9.6 C. Surface temperatures at airport sites in southern Ontario reached 35 to 37 C during this period while the highest dew point temperature reached 17 C. The upper air sounding at Buffalo, New York, at 2000 EDT on May 29, 1988 is shown in Fig. 3. This profile is an example of the large dew point depression that occurred during the episodes. The August 1-5, 1988 episode was the only episode that recorded dew points of 20 C and greater. However the dew point depression was also large. This analysis thus indicates that the episodes occurred with relatively dry air masses.

During each episode, it was also found that the height of the day time boundary layer was capped by an elevated temperature inversion between 1.5 to 2.5 km (Fig.4). The well defined boundary layer contained ozone and its precursors, thus allowing their build up. At night, cooling of the ground resulted in the establishment of a shallow ground-based temperature inversion (100 to 400 m deep), Fig. 4. The polluted air above the inversion was thus cut off from low level scavenging by NOx and was protected from dry deposition; this air is then incorporated in the next day's convective boundary layer. The upper level inversion protected the bulk of the polluted air from vertical dispersion into the free atmosphere, thus prolonging lifetimes of ozone and precursors.

72-hr air parcel back trajectories indicate that air parcels arriving in southern Ontario had previously traversed the major emission source regions of the U.S.. Yap et al. (1988) showed that episodic conditions in southern Ontario for 1983 to 1985 occurred with air flows from the U.S. (more than 95% of the cases during the period). In Fig. 5 trajectories arriving in Toronto at 2000 EDT on August 4, 1988 and at 0800 EDT June 13, 1983 are shown. The average meteorological conditions along the paths are also shown. It is to be noted that there was little wind shear between the 850 mb and 1000 mb levels. This lack of shear allowed the air parcels to transport ozone and precursors with little dispersion into southern Ontario. Yap et al. (1988) also showed that, during the period 1981 to 1984, on 90% of the occasions that there were episodes in Ontario, there were also elevated ozone levels in Michigan. During the July 4-10, 1988 episode, elevated levels of ozone were also found in Michigan and Ohio.

The relatively cloud free conditions encountered along the path of the trajectories were also responsible for the production and transport of the pollutants. It is postulated by Leliveld and Crutzen (1990), that cloud condensation process is an important sink for NOx. During the night NO_3, is converted to N_2O_5 by reacting with NO_2. If condensation occurs, the N_2O_5 almost immediately forms HNO_3. Gaseous nitrate radicals NO_3 produced by the reaction of NO_2 with O_3 is also scavenged by cloud droplets. During cloudless situations, NO_3^- and N_2O_5 could be transformed back into NO_x during the next day. Since NO_x plays an important role in the formation of ozone, the cloud free conditions experienced during the episodes analysed is of great significance to the concentrations measured at the surface.

Conclusions

An analysis of ozone episodes of 4 or more consecutive days duration during the period 1980 to 1991, showed that warm core high pressure systems played an important role in the transport of ozone and its precursors into southern Ontario. Dynamic subsidence, light winds and generally cloud free skies led to high temperatures at all levels of the atmosphere, under the influence of the high pressure systems. Although there was a strong correlation between the 850 mb temperature and high ozone levels, the simultaneous occurrence of light winds, generally cloud free conditions, and the development of the elevated and nocturnal surface-based inversions combined to produce the high concentrations of ozone.

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Pagnotti, V. (1990). Seasonal Ozone Levels and Control by Seasonal Meteorology. Journal of Air Waste Management Assoc. 40, 206.

Yap, D., Ning, D. and Dong, W. (1988) An Assessment of Source Contributions in Southern Ontario, 1979-1985. Atmospheric Environment, 22, 1161.

Yap, D. and Kurtz, J.(1986). Meteorological Analyses of Acid Precipitation in Ontario. Water, Air and Soil Pollution, 30, 873.

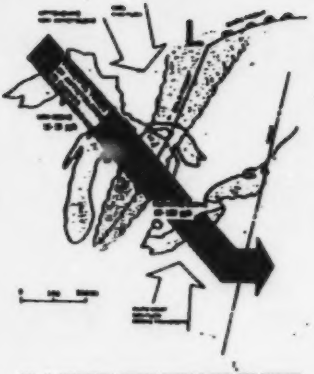
Table 1. Persistent Ozone episodes over southern Ontario - Durations of four or more days (1980-1991).

Duration Days	Period
4	June 23-26, 1980
8	June 10-17, 1983
5	May 27-31, 1988
4	June 12-13, 1988
7	July 4-10, 1988
5	Aug. 1- 5, 1988
4	June 23-26, 1989
5	July 16-20, 1991

Table 2. 850 mb and 700 mb temperatures and dew point temperatures as recorded by radiosondes released daily at 1900 EST from Flint MI. during July 3 -11, 1988.

Date	850 mb		700 mb	
July	T	Td	T	Td
2	13.0	-10.0	4.4	-25.6
3	14.8	0.8	5.4	-25.6
4	18.2	4.8	7.2	-12.8
5	20.8	4.8	7.0	2.0
6	21.8	6.8	6.4	-21.6
7	21.6	9.6	0.8	3.6
8	20.8	8.8	8.4	-1.6
9	20.8	6.8	6.2	4.8
10	12.2	6.2	5.8	4.0

Note that the temperature at both levels increased during the episode and decreased at the end of the episode.



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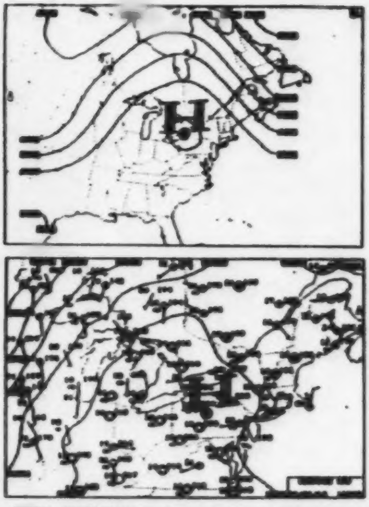

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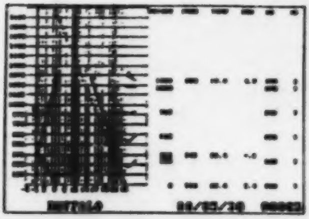

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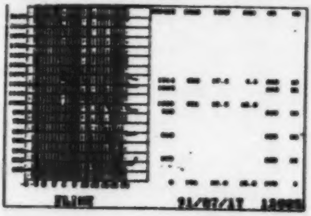

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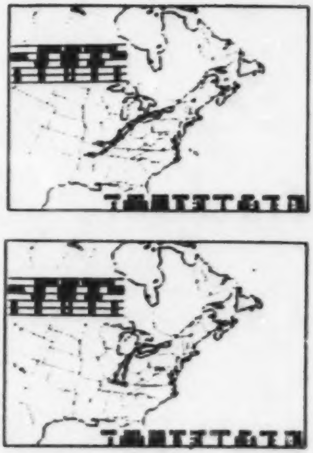

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AP15

AN IN-SITU OXIDATION TECHNIQUE TO REMOVE RESIDUAL CHLORINATED SOLVENTS FROM SOILS.

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Aquifers contaminated with chlorinated solvents pose difficult remediation problems because of the discontinuous residuals formed within soil pores. Removal of the residual by traditional pumping techniques has proven unsuccessful and dissolution of the residual is inhibited by low solubilities. In-situ oxidation may provide an effective remediation technique by converting the residual chlorinated solvents in-situ into less troublesome by-products.

For the analysis of in-situ oxidation, two chlorinated solvents, Perchloroethylene (PCE) and Trichloroethylene (TCE) were selected as common environmental contaminants. These compounds have high surface tension, exhibit low solubility in water and are characterized by a double bond between the two carbons atoms. Oxidation of these chemicals by potassium permanganate involves the cleaving of the double bond and conversion of the carbon compounds into CO_2, MnO_2 as a precipitate, KCl and HCl.

Laboratory scale soil columns were saturated with either PCE or TCE and allowed to drain to residual saturation. Solutions of various concentrations of potassium permanganate were flushed through at rates near typical field conditions. Rates of reaction, effects of the different potassium permanganate concentrations and the conversion process of the PCE and TCE were observed. Analytical work included the analysis of aqueous PCE and TCE, total organic carbon, total organic halide, and Cl^- and the development of mass balances.

Field scale experiments are in progress at CFB Borden within a 1 meter by 3 meter by 2 meter deep sealed sheet piled cell. The Borden sand within the cell has been largely undisturbed to preserve natural hetereogeneities within the soil. An emplaced residual of PCE was established as a source of contamination and a forced gradient has been applied. Solutions of potassium permanganate are being flushed through the PCE contaminated zone with monitoring simillar to the laboratory studies. Destruction of the PCE has been observed similiar to the laboratory soil column experiments.

AP10

GROUNDWATER CONTAMINATION BY ROAD DE-ICING CHEMICALS - IMPLICATIONS OF A SALT BALANCE PERFORMED ON HIGHLAND CREEK, METROPOLITAN TORONTO

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INTRODUCTION

During the past forty years, residents living in the snowbelt regions of Canada and the United States have come to expect bare-pavement driving conditions throughout the winter. As a result, millions of tons of de-icing agents, usually in the form of sodium chloride (NaCl), are applied to urban roads and highways. The general assumption has been that the majority of the applied salt is flushed from the basin every season by rain and snow-melt, and environmental impacts are minimal. There is increasing evidence, however, that a significant proportion of the salt may be retained in the basin, entering the shallow sub-surface and migrating gradually to the water table (e.g. Eisen and Anderson, 1980; Pilon and Howard, 1987). In such cases, serious degradation of groundwater quality could be anticipated.

Concern for contamination by de-icing salts is particularly acute in the Toronto region where well in excess of 100,000 t (Mg) of NaCl are applied to urban roads and highways every year. Within Metropolitan Toronto, major streams regularly contain several hundred mg/l chloride; in winter months values greater than 1000 mg/l are common. The only consolation has been that values of this order have shown little change in recent years and that while values have been unacceptably high, there has been no evidence that the situation will become any worse. Implicit in this attitude is the assumption that problem is under control and that if necessary, a drastic reduction in rates of salt application would dramatically improve the situation.

The wisdom of this view was first brought into question by Paine (1979) who performed a relatively coarse chloride mass balance on the Don River watershed and suggested that as little as 50% of the applied chloride was being removed from the basin annually and that the remainder was being stored in the the shallow sub-surface. Follow up studies by Pilon and Howard (1987) confirmed that concentrations of chloride as high as 14,000 mg/l were accumulating in shallow groundwaters beneath Metropolitan Toronto, thus raising fears that the waters would ultimately enter local streams where serious and uncontrollable contamination would occur.

Recent and current studies at the University of Toronto have been concerned with the impact of urban development on groundwater quality and have focused specially on the movement and behaviour of shallow groundwaters containing elevated concentrations of chloride. An overall goal of the study is to develop a series of numerical models that will permit the movement of de-icing salts in a catchment to be simulated and thereby allow the impact of alternative salting strategies to be evaluated. The success of this model depends in turn, on an understanding of the nature of salt behaviour in a typical urban catchment, and in particular, on an accurate knowledge of the rate at which salt is retained on an annual basis.

The retention rate of de-icing salts in a watershed is best determined using a catchment mass balance approach. In this approach, salt input, represented by the mass of salt applied to the catchment during a specified time frame, is budgeted against salt output in the form of salt loads in the exiting stream. The net difference represents the mass of salt that is stored (retained) within the catchment.

The accuracy of the balance is determined by the quality, frequency and time frame of the data used. In the present study, conducted over three years, this problem has been overcome by the installation of a data logger to collect stream electrical conductivity data at 15 minute intervals. This instrument was calibrated by laboratory and field experiments to provide reliable estimates of chloride concentration. The calibration relationship took the form:

$$Cl^- \text{ concentration (mg/l)} = 0.0000025 * E_c^2 + 0.31 * E_c - 96 \qquad \text{(Eqn. 1)}$$

where E_c is the electrical conductivity in uS/cm at 25°C.

STUDY AREA

The chloride mass balance was performed on Highland Creek basin, one of twelve major subcatchments in the Metropolitan Toronto and Region watershed. The 104 km^2 basin is almost entirely urbanized, with recreational open space along the main Creek valley and some remaining undeveloped land in the extreme northeast. The surface sediments are predominantly silty sand till but recent flood plain deposits occur extensively along the valley floor. The basin is crossed east-west by Highway 401 (12 lanes wide), and by a grid of 2- and 4-lane arterial roads about 1.5-2 km apart. These roads and numerous secondary roads are regularly salted throughout the winter season by five agencies: the Ontario Ministry of Transportation, Metropolitan Toronto, City of Scarborough, Town of Markham and the Regional Municipality of York. The basin receives approximately 17,000 Mg of NaCl road de-icing chemicals each year. This represents approximately 200 g of NaCl for every square metre of the catchment.

Flow in Highland Creek normally varies between 0.3 and 50 m^3/s. Baseflow analyses reveal that groundwater inflows to the Creek vary between 0.3 and 1.2 m^3/s, peaking during the spring and averaging 0.42 m^3/s over the year. This rate represents an average annual recharge to the catchment of 162 mm. If all the applied salt was to enter the sub-surface via recharge, average steady-state sodium and chloride concentrations in groundwater would approach 500 and 800 mg/l respectively.

CHLORIDE BALANCE CALCULATION

The chloride balance was carried out over the period December 1989 to April 1991 inclusive and included three major winter seasons' salting. It was performed by estimating the total chloride input to the catchment over a pre-determined period and subtracting the amount of this chloride leaving the watershed during the same period by stream flow. The difference represents the mass of chloride retained, at least temporarily in surface waters, soils, and subsurface waters. The amount of chloride leaving the basin through stream sediment load is assumed to be negligible.

Chloride Input Data

Road salt is the major source of chloride entering the basin. It is applied as pure salt (NaCl) or as a salt/sand mixture. Daily salt application was determined from the yard records of the five agencies applying salt. Where salt/sanding routes straddled the catchment boundary the total salt applied was apportioned to the catchments on the assumption that rates of application remained consistent along the routes. Total salt application in the study area during the winters of 1988/89, 1989/90 and 1990/91 are shown in Table 1. It is believed that these figures are accurate to ± 5%.

TABLE 1

Annual rates of NaCl application to the Highland Creek catchment

	Sodium Chloride				Chloride
Salting Season	Applied to Roads/ Highways (Mg)	Applied to Parking Lots (Mg)	Domestic Use (Mg)	Basin Total (Mg)	Basin Total (Mg)
1988-89	15031	2104	150	17285	10486
1989-90	16095	2253	161	18510	11228
1990-91	13149	1841	131	15122	9173
Annual Average	14758	2066	147	16972	10295

Also included in Table 1 are estimates of other sources of chloride input. These include the amount of salt applied to parking lots for which it was assumed that rates of application for shopping centre lots were the same as that for major roads, and for other lots one-half this rate. Salt applied to parking lots represented about 14% of the total salt applied. Application by private home-owners was estimated by multiplying the approximate number of single-family residences by an average annual rate of 4 kg/household. This represented less than 1% of the total salt application.

Other sources of chloride are relatively insignificant. Chloride concentration in precipitation around Metropolitan Toronto during 1986 averaged 0.2 mg/l, which converts to approximately 0.1% of the total chloride inputs. Also a calcium chloride de-icing additive is used occasionally in the area but contributes less than 0.1% of the total chloride input. There are no known sanitary-storm sewer interconnections in the basin (Scarborough Works; pers. comm.). Depending on the chemical formulation, fertilizers may contain a significant amount of chloride. However, its potential contribution is not thought to be significant and has not been quantified at this time.

Chloride Output Data

Chloride discharge or "loading" in a stream can be calculated by:

$$Cl = Cm \times Q \qquad \text{(Eqn. 2)}$$

where Cm is mass concentration and Q is stream discharge. This calculation was performed at 15 minute intervals using a Lotus 123 spreadsheet. A summary of the results is presented in Table 2.

TABLE 2

Chloride balance summary for the period November 1st 1988 to October 31st 1991

Salting Season		Total Input (Mg)	Total Output (Mg)	Baseflow Load (Mg)	Corrected Output[1] (Mg)	Salt Output as % of salt applied during salt season	Total %
1988-89	Winter (1 Nov. - 30 April)	10486	2137[2]	486[2]	1651[2]	>15[2]	>34
	Summer (1 May - 31 Oct.)	NIL	2889	867	2022	19	
1989-90	Winter (1 Nov. - 30 April)	11228	4562	1135	3427	31	45
	Summer (1 May - 31 Oct.)	NIL	2699	1089	1609	14	
1990-91	Winter (1 Nov. - 30 April)	9173	3651	1318	2333	26	>26
	Summer (1 May - 31 Oct.)	NIL	-	-	-	-	

- Not determined; [1] Output has been corrected for baseflow load; [2] Data only available for March and April

RESULTS AND CONCLUDING DISCUSSION

Urbanized catchments of the Metropolitan Toronto and Region watershed have, for several decades, received over a hundred thousand tons of de-icing salts annually. For much of this time it has been assumed that most of this salt is flushed from the catchments each season by overland flow and that sub-surface impacts are minimal. However, recent evidence of elevated chloride in groundwater beneath the catchments has suggested that a significant proportion of the applied salt may be retained in the basin each season and therefore be responsible for the observed groundwater quality degradation.

The salt balance performed on the Highland Creek basin of Metropolitan Toronto has generated a large volume of good quality data. Following initial installation problems, the instrumentation proved relatively reliable. Most of the data gaps were due to the failure of Environment Canada flow logging instruments; these data were usually infilled by correlation with data from neighbouring catchments. In total, a full chloride balance was completed for for 26 months extending over three salting seasons.

The results (Table 2) are consistent over the period of study. Each year, during the winter period (1st November to the 30th April) approximately 10,000 Mg of chloride is applied to the Highland Creek catchment. Only 45% of this is removed by surface run-off before the following winter when a a new salting season begins. Most of the chloride removed is flushed from the catchment during the winter in which it is applied. In the 1989-90 salting season, for example, 3427 Mg of chloride left the catchment by overland flow before the end of April representing 31% of the total chloride applied. A further 1609 Mg (or 14% of the total) was removed by summer rain between April 1st and October 30th. Data are incomplete for the salting seasons 1988-89 and 1990-91, but the results available are comparable to those for 1989-90. For example, in 1990-91, 26% of the total chloride applied left the basin during the winter months; in 1988-89, 19% of the total chloride applied was removed during the summer.

If only 45% of the salt applied to the catchment is being removed annually, then the remainder is being stored, presumably in underlying groundwaters. The rate of accumulation will depend on the rate of groundwater movement in the basin. While the total mass of chloride entering the subsurface is greater than the mass of chloride leaving as baseflow to the stream, chloride will accumulate in the groundwater and groundwater chloride concentrations will increase. Eventually chloride in the groundwater will reach a level at which annual baseflow losses will match the amount of chloride entering the sub-surface. At this stage steady-state will be reached and no further deterioration of groundwater or stream water quality will occur. Numerical modelling will allow the rates of change of groundwater and stream water quality to be predicted with more certainty. However, assuming an annual recharge of 162 mm, an aquifer thickness of 50m and a specific yield of 20%, steady state concentration could be achieved within 60 years of initial salt deployment, or approximately 20 years from the present.

When steady state is reached, inflow and outflow of chloride will be in balance and the mass of chloride stored within the basin will remain unchanged. The stored chloride may not be evenly distributed within the sub-surface and water quality stratification will occur depending on the local groundwater flow regime. However, if conditions in the catchment remain the same and present rates of salt application are maintained, calculations suggest that *average* chloride concentrations in groundwaters underlying the basin will reach 426 mg/l. A similar chloride concentration can be expected in stream baseflow, representing a 3-fold increase over present average baseflow concentrations. The value of 426 mg/l is nearly twice the drinking water quality objective of 250 mg/l (aesthetic objective).

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AP17

Microbial Al^{3+} insolubilization: A model for Metal Pollution Control

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Introduction

Aluminum, the most widely occurring metal on earth exists essentially as insoluble polymers of silicates. However it is readily mobilized in bioavailable forms by acid deposition and thus poses a serious environmental and medical threat owing to its deleterious effects on all life forms(1). Aluminum toxicity appears to affect organisms as diverse as plants, birds, fish and humans. Recent clinical findings has linked aluminum uptake to the aging process and the Alzheimer's disease. The latter abnormality has been associated with the deposition of alumino silicates at the core of the senile plaques that characterized demented brains (2).

As part of our study to examine the influence of metals on microbes and to assess their possible use in waste management, we have investigated the interaction of aluminum on Pseudomonas fluorescens ATCC 13525. In this report the detoxification of aluminum via insolubilization is demonstrated.

Material and Methods

The bacterial strain Pseudomonas fluorescens ATCC 13525 was from American Type Culture Collection (Rockville, Maryland U.S.A.). It was maintained and grown in a defined medium containing citrate as the sole source of carbon (3). Aluminum as its chloride salt was complexed to citrate prior to sterilization. At various time intervals, bacterial multiplication was measured by the Lowry method (4).

Analytical techniques:

The citrate assay kit that is based on citrate lyase, lactate dehydrogenase and malate dehydrogenase was utilised in the estimation of citrate decomposition(5).X-ray fluorescence analyses were performed as described in (6). The peak shifts are given in two theta degrees (2θ°) and the intensities in kilocounts per second (kcps). PX1 was used as the analysing crystal. Under these conditions peak indicative of phosphorus and aluminum appeared at 14.15 (2θ°) and 19.21 (2θ°) respectively. Aluminum was quantitated colorimetrically with the aid of aluminon(6).

Results and Discussion

When Pseudomonas fluorescens was grown in a control medium, a cellular yield of 485 µg of protein per ml of culture was observed at stationary phase of growth. The diminution of bacterial multiplication in aluminum enriched medium was dependent on the concentration of the added metal. The decrease in cell yield varied from 16% to 77% in media supplemented with 7.5 mM to 50 mM aluminum (Fig. 1).

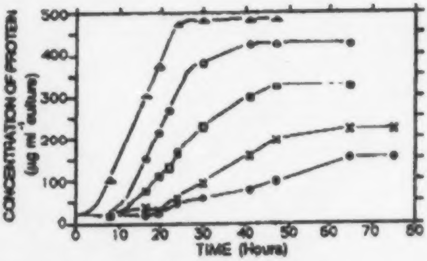

Figure 1: Effects of Aluminum on growth of Pseudomonas Fluorescens ATCC 13525.

Δ—Δ -> no added metal (control medium)
○—○ -> control medium 7.5 mM Aluminum Supplemented
□—□ -> control medium 15 mM Aluminum Supplemented
X—X -> control medium 30 mM Aluminum Supplemented
●—● -> control medium 50 mM Aluminum Supplemented

The biotransformation of aluminum appeared to occur after stationary phase of growth and most of the soluble metal was present as an insoluble residue. Fig. 2.

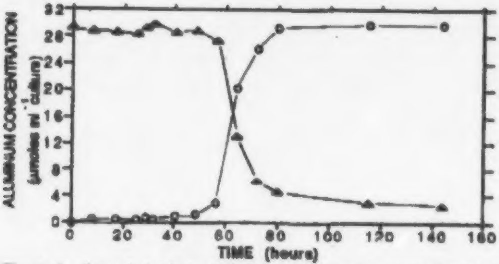

Figure 2: Fate of aluminum during growth of Pseudomonas Fluorescens in 30 mM aluminum culture.

Δ—Δ => supernatant
○ -○ => bacterial cells and pellet

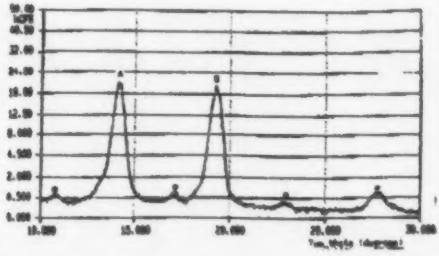

Figure 3: X-Ray Fluorescence Spectrum of purified pellet.

A => phosphorus peak
B => aluminum peak
a => X-RAY peaks

Examination of the precipitate revealed the presence of phosphorus and aluminum only. Peaks attributable to these moieties were evident in the X-ray fluorescence spectrum. (Fig.3).

No citrate was detected after cessation of cellular multiplication.

The data in this report indicate the detoxification of aluminum in Pseudomonas fluorescens is achieved via its transformation into an insoluble phosphorus containing pellet. This appears to be the first demonstration of microbial aluminum bioprecipitation and may indeed provide an interesting model for metal pollution control.

Acknowledgment:

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AP18

Modelling the influence of buildings and obstacles on dense gas dispersion I: Background

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1 INTRODUCTION

A dispersing dense gas forms a low level cloud that is sensitive to the effects of both man-made and natural obstructions. The release of toxic materials is unlikely to occur in the absence of some source structure, adjacent buildings, or buildings between the source and receptors of interest. In fact, nearby structures may be used as release mitigation devices. This study addresses some of the fluid mechanics of the atmospheric dispersion of dense gases, particularly those related to the development of techniques for incorporating the important effects of buildings and obstacles in dense gas dispersion models.

2 BACKGROUND

Whether the release is dense or not, the presence of buildings or obstacles will act to divert the mean flow stream lines and to alter, and in general to increase, the turbulence. There is a reduction of velocity ahead of the obstacle with an increase at the sides and over the top. With bluff obstacles, the flow separates from the obstacle and produces a region of reverse velocity in the lee and a large increase in the turbulence. Material entering this region will be retained there and gradually released, thereby extending in time or space a transient release.

Downstream of the region of reverse flow, both magnitude of the mean velocity deficit and of the turbulence decrease and their spatial extent increases. A further complication is the downstream persistence of vortices aligned with the flow and with a rotation sense that typically produces a mean downward velocity along the axis. When the release is dense, there will be a reduction in any dilution caused by obstacle generated turbulence and also a specific interaction between the buoyancy influenced cloud and the structure.

In summary, the principal effects of structures are: to divert the cloud or plume by altering the background, ambient flow and by interacting with the buoyancy influenced cloud; to enhance dilution as a result of increased levels of turbulence; and, to produce a time lag for the dispersion of the material entering the near wake of the structure.

The limited data available for studying the influence of structures on the dispersion of dense gases is frequently of a specific rather than a generic nature (Dirkmaat 1981, Kothari & Meroney 1982, Krogstad & Petersen, McQuaid 1986, Davies & Inman 1987), and one is left to interpret, and possibly quantify, the various observations in terms of the physical mechanisms listed above. Rottman *et al* (1985b) have considered the interaction of steady and unsteady dense gas flows with obstacles using shallow water equations. They obtained qualitative descriptions of various phenomena anticipated or observed in the field and the laboratory. It was apparent that the shallow water equations were an appropriate tool for addressing the problem of diversion of the cloud by obstacles.

3 DISTRIBUTED OBSTACLES

A typical site will consist of wide variety of sizes, shapes and distributions of buildings and obstacles. It is assumed that at least some part of the obstacles on a typical site can be represented in terms of a distributed array of homogenous roughness.

There has been considerable experimental work on dispersion in the vicinity of obstacles. This work has recently been comprehensively reviewed by Brighton (1989). The available experimental data is interpreted within the context of the integral formulation of dense gas dispersion models. This discussion addresses the principle effects incorporated in these models: advection; horizontal spreading due to negative buoyancy; and, dilution. All of these aspects of the model are presumably influenced by the presence of obstacles.

The observations for homogenous roughness can be summarized as: there is support for the view that an industrial site may be modelled as an equivalent uniform roughness; for homogeneous arrays there is little to suggest that the advection velocity should not be treated in the same manner as for smooth and small roughness surfaces; there is little evidence of any significant effect of the obstacles on the buoyancy induced spreading; the vertical entrainment correlation used in, for example GASTAR, appears to be valid for obstacle arrays; there is little to guide model development on the retention time of dense gas plumes in the wakes of individual roughness elements; and, there is no definitive data has been found, indicating typical vertical concentration profiles within the array.

Note that objective methods for characterizing the surface roughness z_0 have been developed as part of this study.

4 ISOLATED OBSTACLES

In its full generality, the interaction of a dense gas cloud with obstacles presents a formidable modelling problem. However, individually many aspects of this problem are amenable to analysis and this approach is adopted here. Also, from a practical viewpoint, it is possible that many situations of interest can be covered by such individual analyses. This is particulary so for those interested only in a limited number of broadly similar industrial sites.

Our approach is to consider a small number of relevant and commonly occurring situations and to develop models for those cases. Within the framework of the integral model formulation we develop algorithms that will reflect the influence of obstacles on advection, entrainment and for instantaneous releases the 'hold-up' near the obstacle.

The analysis of the influence of structure on dispersion has two purposes: to enable estimates to be made of the concentrations on the structure surface; and, to consider the influence of the structure on the cloud locally and on its subsequent movement and dispersion in order to estimate concentrations at positions downwind.

Speculative analysis in Britter (1982) and generic studies in Konig (1987) and Britter (1989) provide the basis for algorithm development. In addition, there are now many studies, both field and laboratory, which can be used for model assessment. Most of the available experiments have been reviewed by Brighton (1989).

The model algorithms are not intended to describe the complex flow processes near the obstacle but to quantify the net change in the cloud features as the cloud interacts with the obstacle, thereby providing a step adjustment to cloud variables at the obstacle position. This might be used to assess, for example, cloud concentrations on the front and back faces of an obstacle, but care would be required with such an interpretation. The models should retain flexibility so that updated information arising from more sophisticated models or later experiments may be easily added.

Procedures have been developed to handle several cases: two-dimensional fence (solid or porous) at an arbitrary angle to the ambient flow; a confining fence; single fences nearly parallel to the flow; two fences or buildings rows nearly parallel to the flow; single or multiple, isolated, arbitrarily shaped and oriented three-dimensional obstacles upstream or downstream of the source position.

4.1 Trajectory

The presence of obstacles alters the flow field on the site and leads to changes in the trajectory of a gas cloud. The variations in the flow field for a site can be estimated from a generic understanding of the flow around some types of obstacles or from specific site studies. In many cases a precise description of the flow field may not be necessary. Some general statements about the flow field may be all that is necessary to provide significantly improved (and possibly acceptable) modelling accuracy.

The following statements regarding the flow field provide a basis for further discussion:

i) The flow does not go through solid obstacles: the flow goes over wide, shallow structures; and, the flow goes around tall, narrow structures.

ii) The mean flow mean flow might be described by: increased mean flow regions; and, regions of flow recirculation with small internal mean velocity (assumed zero).

iii) The turbulence would be altered only slightly except for: increased turbulence in recirculating regions; and, increased turbulence in the wake, decreasing downstream.

iv) The structures may generate persistent longitudinal vorticity.

The negative buoyancy of the plume may also produce alterations in the trajectory, specifically

v) The plume may be in regions of changed ambient velocity, leading to: an increased plume width when the ambient velocity is small; within a sheltered region leading to enhanced flow upstream, possibly onto the rear face of the building; and, with some longitudinal vorticity above a shallow plume leading to plume bifurcation.

Reasonable estimates of all these effects are currently possible.

4.2 Dilution

When the cloud enters regions with increased mean and turbulent velocities dilution will be increased. The most obvious example of this is the recirculating region behind bluff bodies and the highly turbulent wake further downstream.

Under many conditions the increased turbulent velocities in the recirculating region are adequate to provide effectively complete mixing throughout this region, with the released material behaving as if it were passive.

In other cases a two-layer stratified flow structure is apparent with material in the lower layer undergoing little dilution while the upper layer behaves passively. The possibility of this two-layer structure arising depends essentially on whether the maximum uptake rate from the lower layer is smaller than the source rate.

4.3 Hold-up

When the released material enters regions with small or zero advection velocities it is held there for some time before being released again to move downwind. This aspect of the influence of structures is obviously only relevant to instantaneous and time-varying releases.

The most obvious example of this is the near-wake residence time for material held up within the recirculating region immediately downwind of a structure. A similar description and appropriate parameterization of Brighton (1989) is valid for any recirculating region. This will, in effect, lead to an enhanced longitudinal dispersion of the cloud. In addition we might anticipate a time delay of the centroid of the cloud.

A distinctly different type of hold-up occurs when the material is blocked by an enclosing fence. This occurs when the cloud is very stable and the fence high; the amount of material carried downwind is that which can be detrained from the confining region and when this is less than the source flow, material will accumulate within the constraining fence. This problem lacks a robust description of the detrainment though several approaches are possible.

5 CONCLUSIONS

The review of relevant theory and experiments suggests that procedures can be developed to incorporate the effect of buildings and obstacles on dense gas dispersion within the box model framework.

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VOLUME I

SESSION B

ENVIRONMENTAL EFFECTS

VERBAL PRESENTATIONS

B1

COMPARISON OF LIQUID MANURE SPREADING PRACTICES ON TILE DRAIN WATER QUALITY

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1. INTRODUCTION

Previous research conducted by the ABCA in 1989 and 1990 (Dean and Foran, April 1991) revealed that land application of liquid manure under normal farming practices degrades tile water quality. In eight out of 12 manure spreading events monitored manure components, including bacteria and nutrients, travelled rapidly through the soil column and reached tile drains. This is of concern because the bacterial components of the manure reach surface water, travel downstream and may elevate bacterial counts at public beaches.

Studies by Quisenberry and Phillips (1978) and Aubertin (1971) concluded that in some soils with strong structure and rapid water addition nearly all water flows through the soil macropores and essentially no displacement of soil water occurs. Quisenberry and Phillips (1978) also found that macropores need not extend to the soil surface for flow to occur. In this situation the flow was to a lesser extent. The lower the infiltration rate the longer the retention time in the upper soil zone and therefore, the more efficient the filtering of the bacteria or nutrients. Beven and Germann (1982) suggested that the presence of macropores at the soil surface always increases the infiltration rates because additional surfaces are made available for infiltration into the matrix at depth.

Smith et al. (1985) stated that macropore flow significantly reduces the soils ability to retain bacteria and viruses and increases the potential of groundwater contamination. Almost half of all water borne diseases are caused by contaminated groundwater (Gerba and Bitton, 1984). Although pathogenic bacteria and viruses present in liquid manure may not multiply underground they still may travel considerable distances and survive long enough to be of concern (Bouwer, 1984).

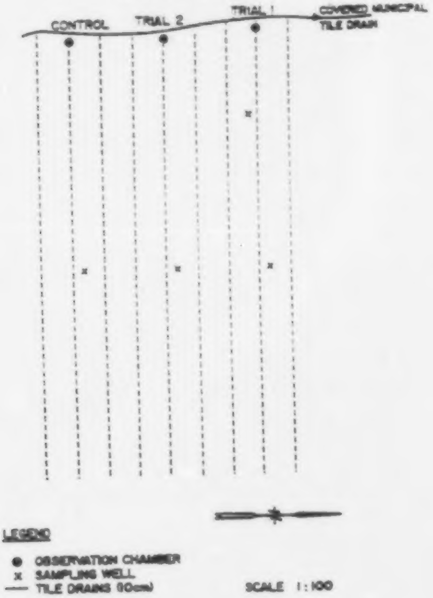
The main purpose of this study is to find possible ways of reducing the impact of liquid manure application on tile drain water and groundwater quality. Spreading on recently cultivated land versus on undisturbed land is compared and spreading using an irrigation gun versus an injector tanker is compared. Disturbing the soil surface prior to manure application may shear off the macropore openings to the surface, slowing down the movement of manure and allowing for filtering of the bacteria and nutrients to occur. The injection method of manure application may smear and close off insitu macropores as the manure is injected. This may result in less contamination of tile drains compared to the irrigation method of application.

2. METHODS

Description of Study Area

The manure application trials are being conducted on a four hectare field of imperfectly drained Perth clay loam soil in Stephen Township, Huron County. This systematically tiled field, with 15 metre tile spacings, has been in a corn/bean/wheat rotation under conventional tillage for the past ten years. Three observation chambers which facilitate taking water samples and discharge measurements from the tile drains were installed in early May 1991. One observation chamber is used on the Control site tile drain while the two others are used for sites Trial 1 and Trial 2. Four sampling wells which vary in depth from 2.2 to 4.1 metres were installed in late May 1991 to monitor groundwater quality in the study area. Figure 1 is a detailed sketch of the study area.

FIGURE I. A DETAILED SKETCH OF THE STUDY AREA


CONTROL
TRIAL 2
TRIAL 1
COVERED MUNICIPAL TILE DRAIN
LEGEND
● OBSERVATION CHAMBER
x SAMPLING WELL
— TILE DRAINS (10cm)
SCALE 1:100

Water and Manure Sampling and Analysis

Samples of the liquid manure are taken from the manure storage prior to manure application. Samples are also taken from collection pans placed in the area of manure application. A minimum of three bacterial and two chemical samples are taken from the manure storages and collection pans so average concentrations can be calculated. Concentrations of bacteria and nutrients in the collection pans confirmed whether or not changes in concentrations of bacteria occurred as a result of pressurization.

Grab samples of water from the tile drains are taken on a weekly basis. More intensive sampling is done on the days of manure application. Daily water samples are taken for approximently one week immediately following spreading. Tile drain discharge measurements are taken at time of sampling.

Grab samples of water from the wells are taken on a weekly basis. Samples are taken daily for approximately one week immediately following manure application. At the time of sampling the water depth in the wells is measured using a water sensor.

Bacterial parameters analyzed in the water and manure include; fecal coliform, fecal streptococcus and *Escherichia coli*. The biotracer, nalidixic acid resistant *Escherichia coli* (EC(NA)) is added to the irrigation pipe prior to pressurization and to the injector tanker in order that their movement could be traced through the soil column and into the receiving water. The EC(NA) is non-enteropathogenic, is easily recovered from water and soil and is not commanly present in the natural environment. The tracer bacteria is injected in concentrations that are approximately equal to the concentrations of the indigenous bacteria found in the liquid waste. Water and manure samples are stored on ice immediately and analysis is performed within 24 hours.

The chemical parameters analyzed for in the tile drain water and manure include: biochemical oxygen demand, suspended solids, free ammonia, total kjeldahl nitrigen (TKN), nitrate, nitrite, total phosphorus (TP), dissolved phosphorus, pH, chloride conductivity and potassium (K). The microbiological and chemical analysis on the water and manure is done at the Ontario Ministry of Environment, Southwestern Region (OME-SWR). Laboratory methods used by the microbiology and chemistry departments are those outlined by the Handbook of Analytical Metods of Environmental Samples (OME 1984b). In addition the microbiology department uses the *Standard Methods for the Examination of Water and Wastewater* (APHA 1985).

Soil Sampling and Analysis

Soil samples for bacterial analysis are taken a few days prior to and within three hours following manure application. Samples are taken using a sterilzed coring device. Soil samples are taken at 1-10 cm, 30-35 cm, and 70-75 cm depths in the soil column. Soil samples are collected in sterile glass jars, stored on ice, and analyzed within 24 hours.

The same bacterial parameters described above for the manure and water are examined in the soil. Again, samples are analyzed at the OME-SWR. The multiple tube fermentation technique is used to determine the bacterial concentrations in the soil (APHA 1985). Results of the examination of replicate tubes and dilutions are reported in terms of the Most Probable Number (MPN).

3. RESULTS AND DISCUSSION

May Spreading Event

Table 1 describes the study area on May 22, 1991. Trial 1, which had been cultivated recently, had a loose friable surface to about a 6 cm depth with no surface cracks. The soil on the Trial 2 and the Control sites had many surface cracks varying in width from 0.5 to 3 mm and many pores <0.5 mm with a few pores with a 1 mm diameter.

TABLE 1. Description of Study Area for the May Spreading Event

SITE	TILE DISCHARGE RATE (L/S)	APPLICATION METHOD	APPLICATION RATE (L/ha)	% SURFACE RESIDUE	SURFACE TREATMENT
Trial 1	0.0032	irrigation	101,000	7	cultivated
Trial 2	0.0032	irrigation	101,000	10	fall plowed
Control	0.0023	--	--	10	fall plowed

Figure 2 shows the EC(NA) loadings in the first 24 hours after manure application to the tile drains at sites Trial 1 and Trial 2. Loading graphs for TKN, TP and K for Trials 1 and 2 have a similar pattern to what can be seen on Figure 2.

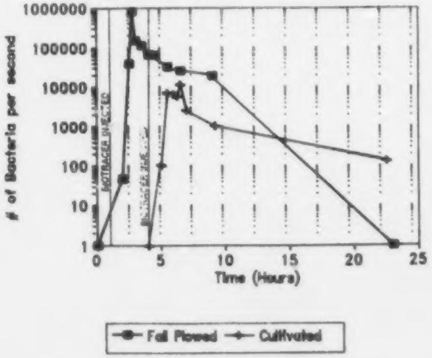


Figure 2. Loads of E.coli (NA)
First 24 Hours After Manure Application

Table 2 shows the average loads of EC(NA), TKN, TP, and K discharging from the tile drains for Trial 1 and Trial 2 in the first 24 hours after manure application as well as the percent of the load applied that reached the tile drains. Trial 2 had a larger loading for all components.

The soil samples taken for bacterial analysis showed no EC(NA) present in the soil prior to manure application. After the application, on the cultivated site no tracer bacteria was found below the surface soil layer while on the fall plowed site the tracer bacteria can be found to the lowest depth measured.

June Spreading Event

Table 3 describes the study area on June 24, 1991. The entire corn field had been scuffled recently for weed control. Scuffling disturbed the soil to about a 5 cm depth. The soil surface in the corn row was undisturbed (12 cm width) and had a few surface cracks varying in width from 1 to 2 cm plus numerous pores < 0.5 mm in diameter. The soil surface between the rows (62 cm width) had no visible surface cracks or pores.

TABLE 3. Description of Study Area for the June Spreading Event

SITE	TILE DISCHARGE RATE (L/S)	APPLICATION METHOD	APPLICATION RATE (L/ha)	% SURFACE RESIDUE	SURFACE TREATMENT
Trial 1	0.0026	injection	81,700	20	scuffled
Trial 2	0.0015	irrigation	121,000	24	scuffled
Control	0.0015	--	--	21	scuffled

Table 2. Loads of Bacteria and Nutrients to Tile Drains for 24 Hours After Manure Application For May and June Spreading Events

	LOADS FROM ISOLATED TILES bacti/day	g/day			LOADS bacti/ha/day	g/ha/day			PERCENT OF LOAD APPLIED THAT REACHED TILE DRAIN			
May 22/91	EC(NA)	TKN	TP	K	EC(NA)	TKN	TP	K	EC(NA)	TKN	TP	K
Trial 1 cultivated	8.6×10^7	1.8	0.17	0.7	2.4×10^8	4.9	0.5	1.9	0.043	0.007	0.0066	0.0026
Trial 2 fall plow	2.4×10^8	24	4.3	14.4	6.7×10^9	67	12	39.5	1.13	0.099	0.17	0.054
June 24/91												
Trial 1 injection	3.4×10^9	53	6.0	47.5	9.1×10^9	119	12	30.4	5.8	0.241	0.28	0.21
Trial 2 irrigation	3.6×10^7	21	1.8	17.5	9.9×10^7	57	4.9	47.9	0.11	0.068	0.06	0.05

Figure 3 shows the Total Phosphorus loadings in the first 24 hours after manure application to the tile drains at sites Trial 1 and Trial 2. Loading graphs for EC(NA), TKN and K for the first 24 hours after manure application for Trials 1 and 2 have a similar pattern to what can be seen on Figure 3.

Figure 3. Loads of Total Phosphorus
First 24 Hours After Manure Application

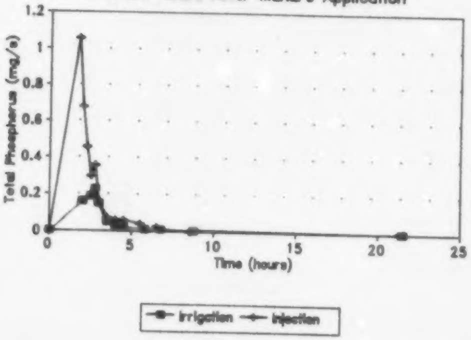


Table 2 shows the average loads of EC(NA), TKN, TP, and K discharging from the tile drains for Trial 1 and 2 in the first 24 hours after manure application as well as the percent of the load applied that reached the tile drains.

No soil bacterial results are available for this application. The sampling wells showed increased bacteria concentrations within five hours of manure spreading initiating for both Trial 1 and 2. The Control Well showed no sign of contamination from the manure spreading event.

4. CONCLUSIONS

Thus far two liquid manure spreading events have been carried out to determine their relative impact on tile drain water and groundwater quality. Cultivation of the land prior to manure application decreased the amount of bacteria and nutrient loading to the tile drain water. The injection method of manure application had a higher loading in the tile drain water compared to the irrigation method. Contamination of the groundwater, however occurred within five hours for both methods.

Two more spreading events are scheduled in 1991. The irrigation versus the injection method of manure application will be compared again as will spreading on recently disturbed land versus undisturbed land. Two spreading events are also planned for the spring of 1992. Further conclusions will be made at that point in time.

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B2

THE EFFECT OF THE EXOTIC ZEBRA MUSSEL (*DREISSENA POLYMORPHA*) ON NATIVE BIVALVES (UNIONIDAE) IN LAKE ST. CLAIR.

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The exotic zebra mussel that has recently colonized the Great Lakes is hypothesized to have a severe impact on the native bivalves especially on the family Unionidae. The impact of the zebra mussel on native Unionidae was examined in Lake St. Clair from 1989 to 1991. Impact is assessed here by the number of dead unionid shells per square meter with attached zebra mussels or with byssal threads. By 1990, 100% of the unionids in the sample area were encrusted with zebra mussels. Heavy infestations of 1000 zebra mussels or more per unionid are common in the study area. A single living unionid was found with 14.4 zebra mussels/cm^2 of exposed surface area, or a total of 1991 zebra mussels was attached to its shell. The mean number of zebra mussels found attached to living unionids in 1989 was 266 and rose to 638 in 1990.

There appears to have been a decline in the unionid populations since the arrival of the zebra mussel. Nalepa (1988) reported 7.8 unionids/m^2 in the area of Pike Creek in the southwest region of Lake St. Clair. In this study the number of living unionids has dropped further from 3.9/m^2 in 1990 to 0.049/m^2 in 1991 from the same study area. In 1990 eleven species were found alive but in 1991 only four species have been found alive to date. The majority (64%) of dead unionids collected in 1991 had zebra mussels or at least byssal threads attached to their shells, suggesting that the zebra mussels are responsible for the decline in the density and diversity of native bivalves from the study area.

In 1990 living unionids were found with massive colonies of zebra mussels on the posterior region resulting in occlusion of the unionid's siphonal region. The growth of zebra mussels between the unionid's valves prevents the total closure of the shell, apparently exposing the unionid to predation and/or parasitism. The weight of some zebra mussel colonies is 3x that of the unionid they are attached to. This extra burden appears to interfere with the unionid's locomotion and balance causing the unionid to topple over onto its side. Many infested unionids have been found dead on their side. The growth rates of unionids in relation to zebra mussel densities are being investigated to further asses the impact of zebra mussels on the Unionidae. The clearance rates of infested and noninfested unionids are also being investigated to determine what effect if any that the zebra mussels are having on the filtration of the unionids.

ENVIRONMENTAL EFFECTS OF HEAVY METALS ON A BENTHIC INVERTEBRATE COMMUNITY IN A PROVINCIALLY SIGNIFICANT WETLAND IN WELLAND, ONTARIO**

by
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Abstract

Changes in benthic invertebrate species composition and relative abundance were plotted as a function of the downstream distance from two point source discharges near a stainless steel manufacturing company in Welland, Ontario. The company discharges approximately 30,000 m^3 day^{-1} into a provincially significant (Class 1) wetlands area of one of 43 Great Lakes Areas of Concern (AOC's). A relatively uncontaminated "control" site was established near the corner of Evan St.and River Road in the city of Welland about 400 m upstream of the company's storm sewer discharge.

Chironomid diversity and species composition were far higher (9-21 genera) at the upstream control site than at any of the downstream stations (0-4 genera). Other benthic invertebrates were also more diverse and more abundant at the control site than at the downstream sites. Pollution tolerant benthic invertebrates such as sludge worms and blood worms dominated the downstream sites. Between 120 to 800 m downstream from the point sources, facultative benthic invertebrates such as isopods, snails and leeches began to replace the pollution tolerant sludge worms and blood worms.

The benthic invertebrate distribution pattern was compared with the heavy metal distribution pattern in the sediments of the Welland River near the site. Nickel (2,900 mg kg-1 dry weight), lead (2,400 mg kg-1 dry weight), zinc (2,200 mg kg-1 dry weight) and chromium (2,100 mg kg-1 dry weight of sediment) were found at downstream sites at 10 to 300 times above upstream ambient concentrations. In 1986, the Atlas Specialty Steels Co. released 31 kg cadmium, 3,545 kg of nickel, and 5,694 kg of chromium into the Welland River (MOE 1987). Cadmium, nickel, and chromium are known mutagens and potential carcinogens. Sites where sediments displayed the highest levels of heavy metal contamination also displayed the lowest benthic invertebrates diversity and densities. Downstream sites that were contaminated with heavy metals displayed the highest proportion of pollution tolerant chironomid genera such as *Procladius cf. bellus* and *Phaenopsectra flavipes*. These same locations displayed the highest percentage of chironomids with mentum deformities.

Twenty five percent of the chironomids removed from the heavy metal contaminated sediments downstream of the Atlas Specialty Steels Co. Ltd. displayed mentum abnormalities. Further downstream, below the Welland Sewage Treatment Plant, the frequency of abnortmalities fell to 17 %. Both of these sites displayed significantly more deformed chironomids than the control site where less than 7% were deformed ($P < 0.01$). By comparison, uncontaminated sediments in Georgian Bay (Lake Huron) displayed chironomid deformity frequencies of 1-3%.

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INTRODUCTION

In freshwater habitats, the most widely distributed benthic invertebrates are the larvae of the chironomid and tubificid worms (Brinkhurst et al., 1968 & Warwick *et al.*, 1987). Frequently, locations which are polluted by man-made contaminants will be associated with an elevated frequency of both of these types of worms (ibid).

Elevated frequencies of chironomid labial plate (mentum) deformities have been associated with agricultural contaminants in lake sediments (Hamilton and Saether, 1971), heavy metal carcinogens such as cadmium and chromium (Wiederholm, 1984; Dickman *et al.*, 1990), sediments contaminated with radioactive substances (Warwick *et al.* 1987), sediments contaminated with vinyl chlorides (Lan *et al.*, 1990) and sediments contaminated by coal tars (Cushman, 1984 & Dickman et al., 1991). Natural populations of chironomids living in areas such as Georgian Bay, which generally have not been impacted by man-made chemicals, display very low (1-3%) frequencies of labial plate deformities (Hare and Carter, 1976).

The role of bottom sediments in rivers and lakes as an absorptive substrate for various heavy metals and polluting hydrocarbons has been suggested by a number of investigators (Black et al. 1979, 1981, Griest 1979). These contaminated sediments make intimate contact with the invertebrates that live on, in and burrow through these sediments. In freshwater habitats, the most widely distributed benthic invertebrates are the larvae of the Chironomid and tubificid worms (Roback 1974, Warwick et al., 1987). Frequently, locations which are polluted by man-made contaminants will be associated with the presence of both of these types of invertebrates (ibid).

Deformities of Benthic Invertebrates Exposed to Mutagens

Many benthic invertebrates are sensitive to teratogens and mutagens. Consequently, many ecologists have attempted to use invertebrate organisms to quantify the level of genotoxins in aquatic sediments (Hamilton and Saether, 1971; Wiederholm, 1984; Warwick, 1985 and 1990; Warwick et al., 1987).

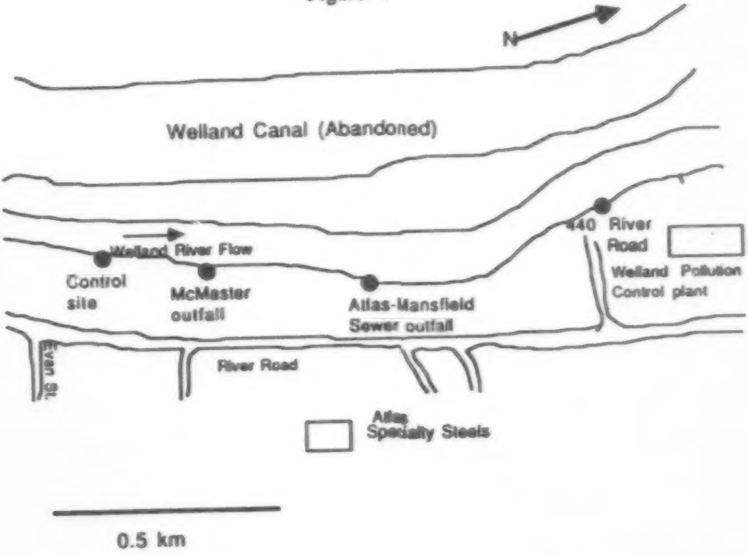
Studies that examined the frequency of deformities of chironomid larvae in polluted sediment led to the use of abnormalities in mouth parts, antennae and chironomid body wall thickness for the detection of genotoxic or teratogenic contaminants (Hamilton and Saether, 1971; Wiederholm, 1984; Warwick *et al.*, 1987; Dickman *et al.*, 1990).

The mouthparts of chironomid larvae are normally symmetrical. Deformed specimens are characterized by asymmetrical labial plates (menta) and mandibular structures. Hamilton and Saether (1971) suggested that different types of pollutants may cause different types of deformities. This differential susceptibility seems to vary among the various chironomid species. Some species are far more sensitive to one group of teratogens than to others (Wiederholm, 1984; Warwick *et al.*, 1987). ***Procladius***, for example appears to be one of the most pollution tolerant chironomid taxa (Warwick, 1991), while ***Phaenopsectra*** is less tolerant and is termed facultative by some dipteran entomologists (Wiederholm, 1984).

Objectives of this Study:

The aim of the present study was to collect chironomid larvae from an International Joint Commission (IJC) area of concern (AOC) in the Niagara River Watershed near Atlas Steels in Welland, Ontario. Sites with known histories of contaminant accumulation were chosen along with an upstream control site (Evan St.). These data were then used to construct a data-base which included the observed frequency of chironomid mentum (labial plate) deformities. The purpose of this data-base was to document benthic invertebrate conditions prior to a sediment clean-up operation so that comparisons with this baseline data set could be made following completion of the proposed Atlas clean-up project.

Figure 1


N
Welland Canal (Abandoned)
Welland River Flow
Control site
McMaster outfall
Atlas-Mansfield Sewer outfall
440 River Road
Welland Pollution Control plant
Evan St.
River Road
Atlas Specialty Steels
0.5 km

Method:

Sampling and sorting

All sediment samples were taken using a standard 15 X 15 Ponar dredge which penetrated the sediment to a depth of approximately 4 cm. The sediment samples collected in the dredge were transferred into a bucket equipped with a 0.75mm mesh sieve. Once the samples were returned to the lab, each sample was sorted, removing the invertebrates.

Mounting and Evaluation

The head capsule of each chironomid was separated from its body, and placed into a beaker containing 10% KOH solution for approximately four to six hour. This was normally sufficient time to allow most of the proteinaceous head capsule tissue to be cleared away from the chitinous mentum.

Each head capsule was mounted on a glass microscope slide using Canada Balsam and xylene. Every slide was coded by Dawn Ralph or Grayzna Rygiel of Brock University in St.Catharines, Ontario. These slides were combined with slides from sites which were not included in this study and coded to ensure that there was no unconscious bias on the part of the examiner during deformity evaluation. The slide mounted chironomids were labelled as either "normal" or "deformed" and the sample was then decoded. A "deformity" in the mentum of a chironomid was characterized by fused teeth, missing teeth, crossed teeth, extra teeth, or teeth of an extremely bizarre size of shape (Dickman et al., 1990);

Results

Table 1
Chironomid Data for Welland River at Evan St.

Chironomid Genera	Evan St.		Evan St. Transect							
			10m		20m		30m		40m	
	Den	%Def	Den	%Def	Den	%Def	Den	%Def	Den	%Def
Ablabesmvia	0	0.0	0	0.0	0	0.0	0	0.0	22	0.0
Clinotanvpus	3	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Dicrotendipes	130	2.1	0	0.0	0	0.0	0	0.0	0	0.0
Einfeldia	3	0.0	66	0.0	0	0.0	0	0.0	0	0.0
Phaenopsectra	283	2.9	0	0.0	0	0.0	0	0.0	66	0.0
Procladius	3	0.0	22	100	0	0.0	0	0.0	0	0.0
C. semi-reductus	5	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Glyptotendipes	11	25.0	0	0.0	0	0.0	0	0.0	0	0.0
Cryptochironomus	3	0.0	22	0.0	0	0.0	0	0.0	0	0.0
Polvpedilum	3	0.0	0	0.0	0	0.0	22	0	22	0.0
Tanvpus	11	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Total	455	3.1	110	20.0	0	0.0	22	0.0	110	0.0
Generic Diversity	1.5		1.4		undefined		0.0		1.4	

Table 2
Chironomid Data for Welland River at McMaster Ave.

Chironomid Genera	McMaster Ave		McMaster Ave. Transect									
			10m		20m		30m		40m		44m	
	Den	%Def	Den	%Def	Den	%Def	Den	%Def	Den	%Def	Den	%Def
Ablabesmvia	0	0.0	22	0.0	0	0.0	22	0.0	156	0.0	0	0.0
Cryptochironomus	0	0.0	22	0.0	89	0.0	22	0.0	133	0.0	133	0.0
Chironomus	0	0.0	0	0.0	0	0.0	0	0.0	44	0.0	0	0.0
Cricotopus	0	0.0	0	0.0	0	0.0	0	0.0	44	0.0	44	100.0
Dicrotendipes	0	0.0	22	0.0	22	0.0	33	0.0	67	33.0	200	0.0
Einfeldia	0	0.0	0	0.0	0	0.0	11	0.0	67	67.0	111	0.0
Orthocladius	0	0.0	0	0.0	0	0.0	0	0.0	22	0.0	0	0.0

Paratendipes	0	0.0	0	0.0	22	0.0	0	0.0	0	0.0	0	0.0
Phaenopsectra	5	0.0	66	0.0	0	0.0	100	0.0	0	0.0	0	0.0
Procladius	5	0.0	44	0.0	22	0.0	67	0.0	400	11.0	0	0.0
Tanypus	0	0.0	0	0.0	0	0.0	0	0.0	22	0.0	0	0.0
Total	10	0.0	176	0.0	155	0.0	255	0.0	955	12.0	488	9.0
Generic Diversity	1.0		2.2		1.1		1.8		2.5		1.9	

Table 3
Chironomid Data for Welland River at 50m Upstream of McMaster Ave

Chironomid Genera	Transect 50m Upstream of McMaster Ave.									
	10m		20m		30m		40m		50m	
	Den	%Def	Den	%Def	Den	%Def	Den	%Def	Den	%Def
Ablabesmyia	0	0.0	44	0.0	0	0.0	0	0.0	0	0.0
Chironomus	622	7.0	0	0.0	0	0.0	0	0.0	89	0.0
Cricotopus	0	0.0	289	0.0	0	0.0	0	0.0	0	0.0
Cryptochironomus	0	0.0	22	0.0	0	0.0	44	0.0	0	0.0
Dicrotendipes	67	0.0	44	0.0	0	0.0	0	0.0	0	0.0
Orthocladius	67	0.0	0	0.0	0	0.0	0	0.0	0	0.0
Phaenopsectra	67	0.0	0	0.0	444	10.0	22	0.0	44	0.0
Polypedilum	67	0.0	0	0.0	0	0.0	0	0.0	22	0.0
Procladius	44	0.0	67	0.0	44	0.0	200	0.0	0	0.0
Total	933	5.0	467	0.0	488	9.0	266	0.0	155	0.0
Generic Diversity	1.6		1.6		0.44		1.0		1.3	

Table 4
Chironomid Data for Weilland River at 50m Downstream of McMaster Ave

Chironomid Genera	Transect 50m Downstream of McMaster Ave.							
	10m		20m		30m		40m	
	Den	%Def	Den	%Def	Den	%Def	Den	%Def
Ablabesmyia	0	0.0	22	0.0	22	0.0	0	0.0
Chironomus	156	0.0	0	0.0	0	0.0	156	29.0
Cryptochironomus	44	0.0	44	0.0	22	0.0	0	0.0
Dicrotendipes	156	0.0	22	0.0	22	0.0	156	0.0
Orthocladius	22	0.0	22	0.0	0	0.0	222	10.0
Phaenopsectra	44	0.0	0	0.0	44	0.0	22	0.0
Polypedilum	67	0.0	22	0.0	0	0.0	0	0.0
Procladius	67	0.0	89	0.0	44	0.0	222	0.0
Total	556	0.0	222	0.0	100	0.0	778	9.0
Generic Diversity	2.5		2.3		2.1		2.0	

Den: Density of chironomids (#/m-2)
%Def: Percentage of Deformed chironomids

TABLE 5
Chironomid Data
Welland River at Atlas Mansfield Sewer outfall
Results for 69 Ponar Dredge Samples

Taxa	Distance from pipe (m)	Number of ind.	Number dredge samples	Density (#m-2)	Deformity Freq. %	Date Sampled
No Chironomids Found	10	0	6*	0	N/A	9/26/89
No Chironomids Found	10	0	4*	0	N/A	10/3/89
No Chironomids Found	15	0	6*	0	N/A	9/26/89
No Chironomids Found	30	0	5*	0	N/A	12/6/89
Phaenopsectra flavipes	30	6	2	134	17	5/01/89
Chaetocladius	30	1	5*	9	0	9/26/90
Phaenopsectra flavipes	60	1	2	22	0	5/1/89
Polypedilum	62	2	2	44	50	9/18/89
Phaenopsectra flavipes	85	1	6*	7	0	9/26/89
No Chironomids Found	85	0	5*	0	N/A	12/6/89
Phaenopsectra flavipes	90	1	2	22	100	5/01/89
Polypedilum	90	1	6*	7	0	9/26/89
Polypedilum	90	1	3*	15	100	10/3/89
Polypedilum	150	1	4*	11	0	9/26/89
Chaetocladius	150	2	4*	22	50	9/26/90
Procladius	150	1	4*	11	0	9/26/90
Chaetocladius	800	1	4*	11	0	9/26/90
Paracladius	800	1	4*	11	100	5/28/90
Procladius	800	2	4*	22	0	5/28/90
Tribelos	800	1	4*	11	0	5/28/90
Chironomus	800	1	4*	11	0	5/28/90
Dicrotendipes	800	1	8*	6	0	6/18/90
Paratendipes	800	1	8*	6	100	6/18/90
Tanypus	800	1	8*	6	0	6/18/90
Cladopelma	800	5	8*	28	20	6/18/90
Cladopelma	800	2	4*	22	50	7/08/90
Totals		34	78	19	26%	

Generic Diversity = 2.8

Table 6

Chironomid Data for Welland River at Downstream 440 River Road

Chironomid Genera	Number of Individuals	Normal Chironomids		Deformed Chironomids		Density (#m-2)
		#	%	#	%	
No Chironomids Found						

Generic Diversity = 0

* sample size <30 chironomids therefore statistical analysis cannot be carried out - no further samples were required by the MOE.

Discussion

Heavy metal contaminated sediments of some rivers and harbours in the Great Lakes region have been found to impact on benthic invertebrate populations at these sites (Sly, 1983; Fallon and Horvath, 1985; Hamdy and Post, 1985; Lum and Gammon, 1985). The concentrations of heavy metals at some locations, including the Atlas Steel's area, have been found to exceed criteria established by the U.S. Environmental Protection Agency (EPA) and the Ontario Ministry of the Environment (MOE, 1989, Redgers *et al.*, 1985). Nickel and chromium, both genotoxic heavy metals (Sax, 1984), were found at concentrations about 2 orders of magnitude above background levels downstream of Atlas Steels Ltd. (Brindle in Dickman et al. 1991).

Changes in species composition and density in benthic invertebrate communities have been correlated with the presence of various toxic materials entering the environment (Buikeman and Herricks, 1978; Wiederholm, 1984). Generally, as the level of sediment contamination increases, a reduction in the complexity of the chironomid community is observed. This reduction is associate with an increase in relative abundance of the pollution tolerant genera, while the less pollution tolerant taxa often disappear (Cairns *et al.*, 1982; Hart and Fuller, 1974). In the present study, the highest incidence of chironomid mentum deformities was observed at sample sites that were located closest to the Atlas-Mansfield discharge pipe (26%) and the McMaster sewer outfall (Transect 3, 9% and 12%). In addition, the dominant chironomid genera collected at these locations were ***Phaenopsectra, Polypedilum*** and ***Procladius***. Each of these genera were classified by Buikeman and Herricks (1978) as pollution tolerant taxa. The absence of all invertebrate life in the 9 Ponar samples taken at the Downstream 440 River Road site was interpreted as indicative of the presence of highly toxic heavy metal contaminated sediments.

Although the percentage of mentum deformities in chironomids collected from the upstream control site (3.1%) was lower than at any downstream location, the generic diversity (1.5) and chironomid density (455/m) were also relatively low. These results indicate that upstream sources of pollution such as heavy metals from the abandoned Welland Iron and Brass Co. might be implicated.

Mechanisms of Genotoxin Deformity Induction

The mechanisms of deformity induction include gene mutations, interference with transcription and translation, disruption of cell division, and metabolic disturbance (Metcalfe and Sonstegard, 1985). Mutagenic or genotoxic compounds cause deformities in animals by disrupting genes (op. sit). Genotoxic substances which are discharged into water systems accumulate in the associated sediments which comprise the habitats for many benthic invertebrate taxa (Buikeman and Herricks, 1978; Wetzel, 1983; Lafont, 1984). Although the absolute concentration of genotoxic pollutants may be very low in water and sediment, the process of "bioconcentration and bioaccumulation" will serve to magnify them in the food chain to many times their inital concentration (Buikeman and Herricks, 1978; Tarkpea et al., 1985). Teratogenic effects rather than genotoxic effects occurred at the PAH contaminated site in the Welland River (Chippawa Creek).

Haydon and Man-Son-Hing (1988) and Kuffler *et al* (1984), noted that calcium metabolism can be blocked by the presence of cadmium. Other heavy metals may also impact on the mentum development of chironomids exposed to elevated levels of these same metals. The increased frequency of mentum deformities observed in the chironomids at the above sites may be due to the formation of calcium deficient menta resulting from the cadmium or other heavy metal contaminated sediments in the area surrounding Atlas Steels.

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Figure Captions

Figure 1. Sample locations along the Welland River are indicated by the circles. The "control site" refers to the Evan St. sample location and the Downstream site is noted by its location on River Road.

B4

A study of the potential for using whole body toxicant residues to predict the effects of time variable exposures in small fish.

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A body residue model of toxicity has been examined as a means of assessing the effects of fluctuating toxicant exposures on small fish. Whole body toxicant residues were found to be a good surrogate of dose and were predictive of effects of time variable exposures to three chlorinated organic compounds in acute studies with fathead minnows. Studies were conducted to determine the potential of a body residue model to predict sublethal toxicity of time variable exposures. Growth studies using fathead minnows were conducted under continuous exposure initially and a threshold body residue was determined as 0.08 - 0.09 mmol/kg pentachlorophenol and 0.2 mmol/kg 2,4,5-trichlorophenol. Acute to chronic ratios based on measured body residues were found to be approx 3.5 for both chlorophenols. Subsequent pulse exposure studies with pentachlorophenol were conducted. Effects on growth were explained using a real time bioconcentration model to predict levels of PCP accumulated in fish. Pulse exposures resulted in toxicant exposures that exceeded LC50 values, however no significant mortality occurred as levels in fish did not exceed the predicted lethal threshold of 0.28 mmol/kg. Actual measured levels of PCP in the minnows by GC-analysis were in excellent agreement with levels predicted by the model.

In these studies, modification of standard ELS test protocols using fathead minnows, to account for differences in feeding and density related effects on growth, significantly improved the sensitivity of the system for detecting toxicity related decreases in growth. Considerations regarding determination of appropriate endpoints as sublethal thresholds and possible considerations for improvements in standard protocols for fathead minnow early life stage studies will be discussed.

85

COMPARISON OF FISH POPULATION IMPACTS OF BLEACHED KRAFT MILL EFFLUENT (BKME) BEFORE AND AFTER INSTALLATION OF SECONDARY TREATMENT.

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ABSTRACT

Jackfish Bay, Lake Superior, has received the primary-treated effluent from a bleached kraft mill for several decades. The mill recently (October 1989) installed a secondary treatment aeration lagoon system to treat its effluent prior to its release. Our data collected in 1989 extended a database initiated in 1988 on the impacts of primary treated effluent on fish populations. These impacts included delayed maturation, smaller gonads, increased liver size, reduced secondary sexual characteristics, increased hepatic mixed function oxidase (MFO) activity and reduced levels of circulating plasma sex steroids. Our 1990 collections have been following these fish populations for evidence of improvements subsequent to the installation of secondary treatment. White sucker collected in August 1990 showed similar MFO activity levels to fish collected in August of both 1988 and 1989. MFO activity in longnose sucker and lake whitefish was also elevated relative to reference fish in August 1990. One year of secondary treatment has not been successful in eliminating BKME impacts on MFO activity. White sucker and lake whitefish exhibited reductions in circulating levels of plasma sex steroids and reduced gonad growth relative to the reference site in 1990. These impacts are identical to ones found in both 1988 and 1989 in the white sucker. The lack of any improvement in the reduced reproductive commitment from 1989 to 1990 in Jackfish Bay suggests that secondary treatment has had no effect on the chronic reproductive impacts of BKME to date. Prior to secondary treatment, Jackfish Bay fish exhibited increased liver size in August relative to two reference sites. During the first year of treatment, liver weights have decreased by up to 50% in lake whitefish and 47% in white sucker. Although MFO induction, gonad size and steroid levels have not recovered during the first year of secondary treatment, there has been dramatic improvements in water clarity in Jackfish Bay and significant reduction in the temperature of the discharge. Studies to identify further improvements following secondary treatment are ongoing.

INTRODUCTION

Pulp mills are the single largest producer of effluent released to the environment in Ontario. The Canadian side of the Great Lakes is the receiver for 19 pulp mills, including 7 on Lake Superior, 3 on Lake Huron, 6 along the Niagara River and 3 on Lake Ontario. The pulp mill industry is under extreme pressure to clean-up their effluent, and all Ontario pulp mills will be required to install a secondary treatment system for their effluent within the next decade. Despite the enormous costs involved in installing a secondary treatment system (>$20-30 M), this has been proceeding without validation that secondary treatment will in fact remove the organic compounds responsible for exerting biological effects, despite the fact that biological effects related to pulp mill effluents have not been clearly identified.

Jackfish Bay has been identified as an area of concern (AOC) by the International Joint Commission (IJC) as it receives approximately 121,000 m^3 d^{-1} of BKME from a mill located in Terrace Bay, Ontario. The bleached kraft mill, produces 1200 air dried metric tonnes (ADMT) of pulp per day, and has released primary treated effluent into Jackfish Bay for several decades. Our 1988 and 1989 collections of white sucker from this area represent detailed baseline studies identifying impacts of this effluent on fish populations (McMaster et al., 1992a,b:; Munkittrick et al., 1991). In October of 1989, the mill installed a secondary treatment aerated lagoon system to treat its effluent prior to its release. Studies conducted in 1990 have followed this white sucker population to evaluate the performance of secondary treatment in mitigating these impacts and have examined other species of fish for similar impacts. Since initiation of the lagoon operation, there have been substantial reductions in release of suspended solids, phosphorus and AOX, a reduction in BOD release by more than 95% (Environment Canada 1989; Ontario Ministry of Environment 1988; Environment Ontario 1991) and elimination of acute lethality of the effluent to rainbow trout (Oncorhynchus mykiss) caged in Jackfish Bay for 7 d (K. Flood, Ontario Ministry of Environment, Toronto, ON, Canada M4V 1P5; unpubl. data). Conditions in Jackfish Bay, including water clarity and temperature of the discharge have also improved dramatically.

STUDY SITE

Jackfish Bay, located along the north shore of Lake Superior, receives BKME from a mill located in Terrace Bay, Ontario. The pulp mill discharges its effluent into the headwaters of Blackbird Creek which receives little dilution between the discharge from the mill, prior to its entry into Moberley Bay (48°50'N, 86°58'W), the western arm of Jackfish Bay, a distance of approximately 15 km. Over the last 40 years Moberley Bay has received either untreated or primary-treated effluent. The mill began operation in 1948 and installed two primary treatment clarifiers during expansion in 1978. Moberley Bay receives no other industrial or municipal effluents, making it an ideal site for studying the impact of BKME on fish populations. For comparison, fish were collected at two different reference sites, Mountain Bay (48°56'N, 87°50'W) and Black Bay (48°30'N, 88°40'W), both which have been used previously to monitor impacts of BKME on Lake Superior fish populations (Smith et al., 1991).

SUMMARY

During all collections in 1989, male and female white sucker exhibited a decreased length and weight and a higher condition factor at the BKME site. This increased condition factor was consistent with an increased water temperature at the BKME site, but was inconsistent with impacts on growth and reproduction. Both sexes exhibited a decreased growth rate and a shift in size distribution towards smaller fish. White sucker exposed to BKME exhibited delayed sexual maturity, smaller gonads, reduced egg size, reduced secondary sexual characteristics and increased liver size. Using an unbiased sampling technique, both males and females were significantly older at the BKME site. White sucker exposed to BKME also exhibited reduced levels of plasma sex steroids (testosterone [T], 11-ketotestosterone [11KT], 17β-estradiol [E] and 17α,20β-dihydroxy-4-pregnen-3-one [17α20β-P]) and elevated levels of hepatic mixed function oxidase (MFO) activity as measured by the metabolism of benzo(a)pyrene, diphenyloxazole and ethoxyresorufin.

Preliminary work on lake whitefish that were collected from Jackfish Bay in 1989, also indicated decreased gonadal growth and increased liver size relative to those at two reference sites. A large number of the BKME fish showed no evidence of gonadal maturation two months prior to the spawning season, indicating an increased age to maturation in whitefish that may exceed that found in the white sucker population.

White sucker collected from Jackfish Bay during August 1990 exhibited similar hepatic MFO activity as recorded in samples collected during August of 1988 and 1989. Secondary treatment has not been successful in eliminating BKME impacts on MFO activity. Hepatic MFO activity was also induced in both longnose sucker and lake whitefish in August 1990. However, samples collected two weeks after a planned mill maintenance shutdown during September 1990, showed no MFO induction in longnose sucker, reduced MFO activity in white sucker and a reduced impact zone for MFO induction in lake whitefish (Munkittrick et al., 1992a). Liver size however, did show improvements following the installation of secondary treatment as white sucker livers declined 47% in females and 22% in males and in whitefish by 37% in females and >50% in males (this trend has not been seen in 1991).

A reduction in circulating levels of gonadal sex steroids has been recorded in fish exposed to BKME in Jackfish Bay during 1989. Neither secondary treatment nor mill shutdown were successful in eliminating impacts of BKME exposure on levels of testosterone and 17β-estradiol in female white sucker and longnose sucker (Munkittrick et al., 1992a). No change in the reduced gonad growth at the BKME site was evident for white sucker and lake whitefish following secondary treatment.

The short duration of MFO induction after shutdown and the persistence of steroid reductions suggest that a) secondary treatment has not been successful in removing "MFO-active" compounds from BKME, b) induction is not related to sediment contamination with persistent compounds, c) the inducing agent(s) are rapidly cleared by fish and that d) effects on steroids may not be directly related to MFO induction. In vivo and in vitro studies in the spring of 1990, suggest that there are other disruptions in the hypothalamic-pituitary-gonadal axis that can account for these lower steroid levels in BKME fish. Although BKME-exposed white sucker are capable of spawning viable eggs, sGnRH failed to induce ovulation in preovulatory fish during a 24 h period, while 10 of 10 fish from the reference site ovulated within 6 h. BKME-exposed fish showed lower plasma levels of both T and 17,20β-P at time 0, while no increase in 17,20β-P was seen after injection of the sGnRH. In vitro incubations of ovarian follicles revealed depressed basal secretion of T and 17,20β-P and diminished responsiveness to human chorionic gonadotropin (hCG). BKME-exposed fish showed lower levels of both free and glucuronated T and 17,20β-P in circulation. These fish however, show similar production of the prostaglandin (PGE$_2$) in ovarian follicles suggesting that there is no general impairment of ovarian maturation (Van Der Kraak et al., 1991).

The ratio of steroid production between sites is the same as the ratio in the blood between sites, suggesting that induced hepatic MFO activity is not associated with altered plasma steroid clearance rates. Independence of hepatic MFO activity and steroidal abnormalities is also suggested by experiments showing a) no change in clearance of injected steroid and b) persistent depression of circulating steroids during spawning and mill shutdown, when MFO levels are not induced.

During our thorough investigation of the lake whitefish populations response to BKME exposure, more than 20% of the whitefish collected at the BKME site exhibited lateral, slash-like lesions which penetrated the body cavity. Histological examination revealed no evidence of an infectious etiology, and the wounds could not be accounted for by known causes (Munkittrick et al., 1992b). Similar lesions were found in 1991 near a second BKME discharge.

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B6

CARCINOGENICITY TESTING OF BLEACHED KRAFT MILL EFFLUENT USING *IN VIVO* AND *IN VITRO* ASSAYS,

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In vivo and *in vitro* assays are being used to determine whether bleached kraft mill effluents (BKME) have the potential to be carcinogenic to fish. BKME extracts were prepared by column chromatography with XAD resins. Non-polar to medium polarity compounds were extracted using XAD-4 resin, and polar compounds were extracted using XAD-7 resin. Mutagenic activity was detected in XAD-7 extracts using the *Salmonella* fluctuation assay, but there was a negative response in the *Salmonella* plate-incorporation assay. The XAD-4 and XAD-7 extracts induced slightly elevated activities of hepatic aryl hydrocarbon hydroxylase (AHH) and ethoxyresorufin-O-deethylase (EROD) in *in vivo* tests with rainbow trout. However, these extracts were hepatotoxic to the trout at high doses. BKME extracts were tested for carcinogenicity using an *in vivo* assay with rainbow trout. Gross observations of tumour incidence indicated that XAD-4 extract enhanced the carcinogenic response to a potent hepatocarcinogen, aflatoxin B_1, but the extracts were not carcinogenic themselves. Histological evaluation of the carcinogenicity data is underway.

B7

MULTIFACTORIAL CAUSES OF POLLUTION-ASSOCIATED NEOPLASMS IN FISH IN LAKE ONTARIO.

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ABSTRACT

Environmental and water quality can be monitored by epidemiological evaluation of pollution-associated diseases of wild fish, provided that it is based on an understanding of the various causative factors involved in the pathogenesis of the diseases monitored. Our studies have evaluated the influences of naturally occurring liver diseases on the susceptibility of white suckers *(Catostomus commersoni)* to environmental carcinogenic polyaromatic hydrocarbons (PAH), especially benzo[a]pyrene (B[a]P). White suckers from urban/industrial locations in western Lake Ontario have higher concentrations of metabolites of polycyclic aromatic hydrocarbons (PAH) in bile than do fish from clean sites. White suckers from some PAH-polluted locations also have an elevated frequency of liver tumors, whereas some other fish species in the same polluted habitats appear to be resistant to tumor development. We have demonstrated that bottom-feeding fish including white suckers, brown bullheads, European carp and channel catfish have strong glutathione S-transferase (GST)-dependent DNA-protective activity against DNA-binding metabolites of B[a]P, namely B[a]P-7,8-diol-9,10-epoxide (BPDE) and B[a]P-4,5-oxide (BPO). By comparison, liver GSTs of rainbow trout, lake trout, salmon and various terrestrial mammals, including humans, are less able to protect DNA from these reactive PAH metabolites. White suckers from both clean and polluted sites have a chronic inflammatory disease of bile ducts (cholangiohepatitis) associated with parasitic protozoa (Myxosporea), digenetic flukes *(Sanguinicola sp)* and larval nematodes (Acuarioidea). These parasitic diseases are associated with a high frequency of obstructions of bile ducts, resulting in segments of liver with reduced activity of hepatic GST activity, a detoxification system that is important in biliary excretion of PAHs and B[a]P in these fish. We demonstrated that various substances that accumulate in the liver after bile duct obstruction, including some bile acids, bilirubin, biliverdin and hematin, are potent inhibitors of hepatic GSTs in white suckers. Bilirubin and hematin also inhibited glutathione conjugation of B[a]P-4,5-oxide mediated by GST proteins from white sucker liver. However, in white suckers given small quantities of ^{3}H-B[a]P, levels of labelled DNA adducts in obstructed lobes were very low and similar to levels in more normal areas of liver. These studies suggest that white suckers and other bottom-feeding fish are remarkably resistant to B[a]P and that naturally-occurring parasitic liver diseases might interfere with detoxification of some PAHs. The hypothesis that multiple factors are involved in the susceptibility of white suckers to pollution-associated liver carcinogenesis has important implications for efforts to monitor environmental carcinogens by tumor surveys in fish in the Great Lakes.

INTRODUCTION

The impact of urban/industrial pollution of aquatic environments can be monitored by the epidemiological and mechanistic studies of diseases of wild fish (1-5). For example, the prevalence of liver tumors (neoplasms) in various species of bottom-dwelling fish is an indication of pollution-associated changes in marine (2, 6-10) and freshwater environments (1,11-14) but such studies have not yet successfully identified the most carcinogenic contaminants putatively involved in the pathogenesis of these neoplasms. Tumor prevalences provide a geographical indication of changes, including environmental carcinogens, within regions of an ecosystem, but do not necessarily measure the risk to other species within the same ecosystem. In terrestrial mammals, including humans, liver carcinogenesis is a complex response to various environmental and endogenous factors, including infectious diseases, genetic susceptibility, behavior, diet and also food-borne carcinogens from their environment (15-16). This suggests that an understanding of the environmental significance of pollution-associated liver neoplasms in fish cannot be reliably developed from selective evaluation of effects of pollutants without regard to other contributing influences (14). It also implies that responses of fish to pollutants that are reliably implicated as risk factors for their tumor susceptibility cannot be readily extrapolated to other species of fish or terrestrial species until more is understood about the context of this susceptibility. Accordingly, environmental scientists working with industries, regulatory agencies and other interest groups need to develop a clearer rationale for interpreting tumor prevalence data in fish as indicators of ecosystem stresses, or as measures of potential health risk risk to humans and other species.

Cancers result from a series of insults in the context of changes in the host ability to resist these insults (17). Some changes in resistance obviously relate directly to exposure levels to substances with genotoxic or promoting effects on tumor development. In this situation, problems can directly relate to an imbalance between the ability of the host to resist carcinogenic responses (eg avoidance, detoxification, and repair of promutagenic insults). However, for many DNA damaging carcinogens of environmental significance (eg polycyclic aromatic hydrocarbons (PAHs), aflatoxins, etc), most normal individuals are unlikely to be exposed to sufficiently high environmental levels to saturate these constitutive resistance mechanisms (17,18). Similarly, non-genotoxic politants (such as organochlorines, especially PCBs, dioxins, etc) that are carcinogenic in laboratory animals exposed at high chronic rates substances, evidently act by mechanisms that do not operate at very low levels of exposure (17). Variation in susceptibility can also be due to factors that increase (induce) or reduce resistance. For example, persistent chemicals that induce cytochrome P-450-dependent monooxygenases and phase II detoxification enzymes, increase the ability to resist DNA damage by many genotoxic carcinogens that are detoxified by the induced systems (17). More important from the environmental perspective are influences that actually compromise these constitutive and inducible resistance mechanisms to environmental chemicals. For example, there are well recognized differences in resistance to genotoxic (18) and non genotoxic carcinogens (17) among species, and also among individuals with genetic polymorphic differences in expression of crucial enzymes involved in detoxification or DNA repair (19,20). Furthermore, concurrent liver disease due to viral or parasitic infections (20,21) can decrease function of various detoxification or repair enzymes, either by increasing the load of hepatic waste products that inhibit them (22), or by eliciting regenerative proliferation of cells that are more likely to become mutated when their repair mechanisms are overloaded (17,20). Finally, during the pathogenesis of liver cancer in mammals and fish, preneoplastic cell populations develop; some of these have induced resistance to carcinogens, whereas other clearly lose their constitutively expressed glutathione S-transferases (GSTs) that are essential in resistance to DNAS damaging PAHs and aflatoxin (14,18,23,24).

This paper describes our recent investigations of various factors that might influence the susceptibility to liver neoplasia in various bottom-dwelling species from the Great Lakes particularly white suckers (*Catostomus commersoni*) from industrially-polluted western Lake Ontario. These studies suggest that concurrent liver disease in white suckers contributes in several ways to an interference with strong constitutive GST-dependent resistance to benzo[a]pyrene (B[a]P), a representative of the PAH class of environmentally important carcinogenic pollutants that are known to be more abundant in sediments in locations where pollution-associated liver tumors have been recognized in bottom-feeding fish (6-10,12,13,25,26). Our findings place some complexity on interpretations of significance of tumors in wild fish, but provide some guidance with respect to the judgements of extended environmental risk to humans and ecosystem health, and also with respect to distictive properties of the as yet unidentified environmental substances most likely involved in carcinogenesis in these fish.

MATERIALS AND METHODS

Reagents. ^{3}H-Benzo(a)pyrene (^{3}H-BaP, specific activity 56 Ci/mmol) was a product of New England Nuclear (Boston, MA). (±)-r-7,t-8-dihydroxy-t-9,10-epoxy-7,8,9,10-tetrahydro [1,3-^{3}H] benzo[a]pyrene (anti) (^{3}H-BPDE, specific activity 439 Ci/mmol) was obtained from Chemsyn Science Laboratories, Lenexa, KS. (±) Benzo(a)pyrene-4,5-dihydroepoxide (BaP-4,5-oxide) was purchased from the NCI Chemical Carcinogen Repository, (Kansas City, MO). Chenodeoxycholic acid (99% purity), deoxycholic acid, bilirubin, biliverdin, hematin, GSH, sodium dodecyl sulfate (SDS),1-chloro-2,4-dinitrobenzene (CDNB), 2-phenoxyethanol and calf thymus DNA (type 1) were purchased from Sigma Chemical Co. (St. Louis, MO.). NADPH, ribonuclease (RNase A) and protease (Proteinase K) were products of Boehringer-Mannheim Biochemicals (Dorval, Quebec, Canada). Methanol (HPLC grade) and trichloroacetic acid were obtained from Fisher Scientific Co. (Nepean, Ontario, Canada). Hydroxyapatite (DNA grade, Bio-Gel HTP) was obtained brom Bio-Rad Laboratories (Mississauga, Ontario, Canada). All other chemicals were of reagent grade.

Animals and Treatments. Liver samples from brown bullhead, carp, catfish, sculpin, and perch were generously provided by J. Fitzsimons of the Canadian Centre for Inland Waters, Burlington, Ontario or by I. Smith, Ontario Ministry of the Environment, Rexdale, Ontario. Samples from trout and salmon were obtained from H. Ferguson, Fish Pathology Laboratory, Department of Pathology, University of Guelph, Guelph, Ontario. Adult male white suckers (n=241) were caught from the Humber River (Toronto, Ontario, Canada) during their spring spawning migrations and were maintained for 1 week in laboratory holding tanks in clean well water at 10°C. Laparotomies were performed on fish under anesthetic (2-phenoxyethanol, 5ml/liter water) in order to detect segmental liver obstructions. These obstructed regions occurred consistently in the most distal liver lobes and were easily identified because they were stained a dark brown-green color due to retained bile pigments. The existence of segmentally obstructed liver lobes in these fish provides a unique opportunity to compare the metabolism and genotoxicity of carcinogens in areas of liver affected, to a greater or lesser degree, by cholestasis. For studies on the binding of BaP metabolites to liver macromolecules *in vivo* , fish with obstructions were orally administered ^{3}H-BaP (0.2 µmol/kg of body weight; 2 ml of corn oil/kg of body weight) 1-2 days after surgery. Fish were killed 24 hours later and samples of obstructed and adjacent unobstructed liver were separated and frozen for adduct analysis. Necropsies were performed on other fish and liver tissue from those with segmental obstructions was used to prepare cytosol for analysis of GST activity and for the extraction of bile acids. Cytosol was also prepared from the liver of fish without gross evidence of obstructive bile duct disease for use in enzyme inhibition assays and in the affinity purification of GST.

Histopathology and Isolation of Parasites. This study did not focus on the prevalence or histopathological characteristics of hepatocellular or cholangiocellular neoplasms in white suckers as this topic has already been covered in other studies (14, 24). Histopathological studies were performed on white sucker liver in order to assess the prevalence of inflammatory liver disease and parasite infestation in fish from polluted and reference sites in the Great Lakes. Histological sections of liver from white suckers from in Lake Ontario (Humber R., N=46 and Ganaraska R., n=40) and Lake Huron (South Bay, N=47 and Spanish R., N=46) were generously provided by Dr V. Cairns, Canadian Center for Inland Waters, Burlington, Ontario, Canada. Liver tissue was fixed in 10% formalin and 5µm paraffin sections were stained with hematoxylin and eosin (H&E). Sections were examined for the presence of inflammatory lesions which were broadly categorized as either cholangiohepatitis or cholangiofibrosis by criteria described in the results. The lesions were graded on a scale of 0 to 4 (0: no visible lesions; 1: mild; 2: moderate; 3: marked; 4: severe) according to the severity of the lesions. Evidence of parasitism was assessed by quantifying the number of parasites or parasitic granulomas visible per section. The location of parasites (i.e. within bile ducts, blood vessels or hepatic parenchyma) and evidence of parasite-associated inflammation (ie migratory tracts) was also noted. Parasites were also isolated from liver tissue by manual extraction under a dissecting microscope or by pepsin digestion using a Baerman's apparatus.

Preparation of Hepatic Cytosols and GSTs. Liver tissue from the various species of fish and from obstructed and adjacent unobstructed liver from white suckers with gross evidence of obstructive bile duct disease were collected on ice, minced, and homogenized in 3 volumes of 0.25 M sucrose (pH 7.4), at 4°C, containing 1 mM EDTA and 25 mM Hepes. Cytosol was prepared as the final supernatant of centrifugation at 10,000g (30 min, 4°C) and 100,000 g (60 min 4°C) (18). Cytosol, from the livers of suckers unaffected by obstructive bile duct disease, used for GST purification by affinity gel chromatography, was dialyzed for 18 hr (12-14 kDa cutoff) against 10 mM Tris-HCl containing 50 mM NaCl (pH 7.8, at 4°C) and applied to a column (1X20 cm) containing *S*-hexylglutathione-Sepharose 4B (Pharmacia, Etobicoke, Ontario). Following extensive washing with 200 mM NaCl, GSTs were eluted with the wash buffer containing 5 mM *S*-hexylglutathione (18). The fractions exhibiting GST activity by 1-chloro-2,4-dinitrobenzene (CDNB) conjugation were pooled, dialyzed for 24 hr against 10mM Tris-HCL (pH 7,5) and stored at -70°C. The affinity-purified GST preparations contained only bands in the 24-28 kD range present in silver-stained polyacrylamide electrophoresis gels, the purity of which was confirmed by western immunoblot analysis (23).

Enzyme Assays and Inhibition Studies. The activity of cytosolic GST and affinity purified GST towards the substrates CDNB and BaP-4,5-oxide was determined. GST activities using CDNB (0.5 mM, pH 6.5) as a substrate were measured at 25°C by the spectrophotometric method of Habig *et al* (28). Specific activities were expressed as µmol CDNB/min/mg protein. The assay of GST activity towards BaP-4,5-oxide was based on a method described by Eaton and Stapleton (29). The effect of chenodeoxycholate, deoxycholate, bilirubin, and hematin on the activity of sucker hepatic GSTs towards CDNB was measured by comparing the reaction rate in the absence and the presence of the inhibitors. The effect of bilirubin, hematin and CDCA on cytosolic GST activity using BaP-4,5-oxide as a substrate was also determined. The enzyme (25 µl containing 40 µg cytosolic protein or 2.5 µg of affinity purified GST) was preincubated with the inhibitor for 5 minutes prior to the addition of substrates. In the CDNB assays, at least five different concentrations of inhibitors, in the µmolar range, were used in the assays and the I_{50} values (the concentration giving 50% inhibition of enzyme activity) were determined from plots of remaining activity vs inhibitor concentration. Because of the limited solubility of CDCA, 2.0% (v/v) methanol was included in the assay for this bile acid. Hematin, biliverdin and bilirubin were dissolved in 10 mM NaOH and all solutions were protected from light. The volume of the additions of inhibitor solutions was 20 µl. Control experiments were performed in the absence of nonsubstrate ligand but included appropriate concentrations of methanol or NaOH carrier solutions. Activities represent the average of 3 determinations.

Separation of GSTs on Polyacrylamide Gels. Polypeptide subunit profiles of cytosol and purified GSTs were analyzed by SDS-polyacrylamide (12%) gel electrophoresis (SDS-PAGE) as described by Rushmore et al., (30). All gels were stained with silver nitrate following the procedure described by Wray et al. (31).

DNA Binding Assays. The DNA protective activities of cytosols from livers from various species of freshwater fish including brown bullhead, carp, catfish, sculpin, trout, perch as well as obstructed and adjacent unobstructed and affinity purified GSTs from white sucker liver were assayed in an *in vitro* DNA binding procedure similar to that described by Quinn et al. (18). Each 1-ml reaction mixture contained 0.1 M K-phosphate buffer (pH 7.4), 0.1 M sucrose, 0.5 µCi ^{3}H-BPDE or ^{3}H-B[a]P-4,5-oxide (1 µM) dissolved in 20 µl of tetrahydrofuran/triethylamine (19:1), 0.2 mg calf thymus DNA, NADPH (2mM), 1.6 mg cytosolic protein (i.e. cytosol from obstructed or adjacent unobstructed liver) and various concentrations of dialyzed affinity-purified liver GSTs with or without GSH (2.5 mM). Samples were incubated for 8 min at 25°C, and then extracted three times with chloroform/isoamyl alcohol (10:2, v/v). Ethanol-precipitated DNA was collected by centrifugation, washed with ethanol, and dissolved in 1 ml 10 mM Tris-HCl/1 mM EDTA (TE buffer, pH 7.4). DNA was purified by incubation with ribonuclease A and proteinase K, and then extracted, precipitated and redissolved as described above. The DNA in solution was quantified by 260 nm absorbance, radioactivity was measured and ^{3}H-BPDE bound to DNA was expressed as pmol bound/mg DNA.

BaP metabolites bound to sucker hepatic DNA *in vivo* were also measured. BaP-modified DNA was isolated from normal and obstructed liver tissue by hydroxylapatite chromatography according to the method described by Adriaenssens et al. (32). The DNA was quantified by 260 nm absorbance using the relationship 1mg DNA=50 A_{260} units. The purity of the final preparation was judged by the absorbance ratio of A260 nm:280 nm which consistently ranged from 1.8-2.0. BaP-derived radioactivity was then assessed in the DNA solution by direct liquid scintillation counting (LSC) and the specific binding of BaP to DNA was expressed as fmol BaP/mg DNA.

Protein Isolation and Quantification of BaP Covalently Bound to Protein. Protein was isolated from the CIP extract obtained during the isolation of DNA as described by Stowers and Anderson (33). BaP-derived radioactivity in the protein solution was then assessed by LSC. The covalent binding of BaP to protein was expressed as fmol BaP/mg protein.

RESULTS

Gross and Histologic Lesions. Many white suckers had a diffuse inflammatory proliferative reaction along portal tracts, which is subsequently referred to as cholangiohepatitis. Liver affected with cholangiohepatitis had diffuse lesions that were consistently centered on major bile duct systems. Major portal tracts were prominent and tortuous with markedly hyperplastic biliary epithelium frequently folded into papillary lumenal projections. Duct lumens often contained protein- and/or mucus-rich material together with exfoliated necrotic epithelial cells and some leukocytes. Surrounding these biliary tracts was an associated marked chronic periductal inflammatory reaction characterized by a mixed mononuclear cell infiltrate together with a mild to severe degree of periportal fibrosis. There was occasionally periportal proliferation of small cholangioles that extended into the hepatic parenchyma.

A less frequent but distinct process, subsequently termed cholangiofibrosis, occurred mainly as relatively discrete focal lesions in the peripheral regions of the liver; the long narrow distal lobes being most frequently affected. Some of these distal obstructed lobes were dark green segments that were readily distinguished from the tan colored proximal adjacent unobstructed liver. The more chronic and fibrotic lesions appeared as discrete pale foci (2-20 mm) present within obstructed lobes. Histologically, affected areas had focal segmental proliferations of small cholangioles, accompanied by moderate to severe interductal fibroplasia . In the more severely affected regions, there was marked hepatocellular atrophy with few residual hepatocytes recognizable among the cholangiofibrotic reaction. Melanomacrophage centers comprised of greatly enlarged phagocytes containing yellow brown cytoplasmic pigment were prominent in these areas. Leukocytic infiltrates were minimal except in the vicinity of migratory parasites, encapsulated granulomas or concurrent areas of cholangiohepatitis. The distribution and histologic appearance of the cholangiofibrotic lesions was consistent with a segmental bile duct obstruction.

Several different parasites were observed both grossly and histologically in the livers of these fish. Protozoal cysts (*Myxozoa: Myxosporea*) were visible within major bile ducts the epithelium of which was hyperplastic. Nematode larvae (*Spirurida: Acuarioidea*) were located within acutely necrotic areas of hepatic parenchyma and were associated with infiltrates of granulocytic and mononuclear inflammatory cells or were present within encapsulating granulomata. Flukes *(Diginea: Sanguinicola)* were present mostly in portal veins but occasionally within areas of acutely necrotic tracts in the hepatic parenchyma .

Hepatocellular neoplastic lesions ranged from small round or irregular foci of phenotypically altered (basophilic) hepatocytes to larger hepatocellular neoplasms that were expensive or often locally invasive within the liver. These lesions were composed of polygonal cells with a higher nucleus to cytoplasmic ratio and less cytoplasmic differentiation than normal hepatocytes. Lesions corresponding to foci of hepatocellular alteration, were occasionally visible grossly as small (2-10 mm) dark brown spherical areas scattered throughout the liver. Biliary neoplasms consisted of either bile duct adenomas, typically discrete nodules of irregularly arranged ducts within a connective tissue matrix, or carcinomas, typified by extensively invasive, poorly differentiated, irregular duct-like structures.

The prevalence of inflammatory bile duct disease in white suckers was determined by histological examination of sections of white sucker livers from two polluted and two reference sites in the Great Lakes. Quantification of mean histological scores reflecting the severity of lesions of cholangiohepatitis and cholangiofibrosis revealed that inflammatory bile duct disease is widespread in white suckers throughout the Great Lakes (Fig.1). While some livers from all sites had evidence of Sanguinicola, Myxosporea, and Spirurid parasitic infestations, there were no obvious differences in the frequency of infestations among types of parasites and sites.

Assays for GST Activity and Expression. The hepatic cytosolic GST activities (CDNB) from various species fish including brown bulhead, white sucker, catfish, sculpin, perch, trout and salmon are presented in Fig. 2. Hepatic cytosolic GST activity varied significantly in the various species examined . Generally, the GST activity was greater in benthic fish species compared to pelagic fish. The influence of bile duct disease and cholestasis on cytosolic GST activity was also determined. GST activity (CDNB conjugation) of cytosol prepared from obstructed and adjacent unobstructed liver was examined. GST activity in cytosol prepared from obstructed liver (mean ± SE, 0.25 ±0.08) was 45% lower ($p<0.05$) than the activity in cytosol prepared from adjacent unobstructed liver (mean ± SE, 0.55 ± 0.08) (Table 1). Densitometric analysis of polypeptide bands corresponding to GST proteins (24-28 kD range), separated from cytosol by SDS-PAGE, revealed that the major cytosolic GST subunits were similarly expressed in obstructed and adjacent unobstructed liver.

The influence of various endogenous nonsubstrate inhibitors including chenodeoxycholic acid, deoxycholic acid, bilirubin, biliverdin and hematin, on the activity of cytosolic and affinity purified GSTs towards CDNB and BaP-4,5-oxide was determined *in vitro*. The results are presented in (Table 2). GST activity was inhibited by µmolar concentrations of these inhibitors in a dose-related fashion. Hematin was the most profound inhibitor of hepatic GSTs with an I_{50} value of less than 1 µM. Preincubation of hepatic cytosol with µmolar concentrations of bilirubin resulted in dose-related reductions in GST activity towards BaP-4,5-oxide, however, CDCA and hematin had no effect.

Binding of BaP to DNA and protein *in vivo* and *in vitro*. The degree of protection provided by cytosol from liver of various benthic and pelagic fish species against binding of BPDE or B[a]P-4,5-oxide to DNA was examined *in vitro*. Liver cytosol from pelagic fish species provided less protection against binding of BPDE and B[a]P-4,5-oxide to DNA compared to cytosol from the liver of benthic species (Fig. 3). The effect of cholestasis on GST-mediated detoxification of electrophilic BaP metabolites was assessed in various binding assays *in vivo* and *in vitro* (Table1). Hepatic affinity purified and cytosolic GSTs from white suckers provided dose-related protection against the binding of the ultimate carcinogenic metabolite BPDE to DNA *in vitro*. The reduced DNA binding provided by affinity-purified cytosolic GSTs in the presence of GSH was not evident in the absence of GSH. The protective effect of cytosol, derived from obstructed or adjacent unobstructed liver, against the binding of BPDE to DNA *in vitro* was also analyzed (Table 2). Cytosol from adjacent liver had slightly stronger protective activity against DNA binding by BPDE (16.4 pmol BPDE/mg DNA ±1.3, $p<0.08$) than cytosol from obstructed liver (20.6 pmol BPDE/mg DNA ±1.8). There was no statistically significant difference in the degree of binding of BaP metabolites to macromolecules (either protein or DNA) in obstructed liver and adjacent unobstructed liver (Table 1).

DISCUSSION

The results of this study clearly indicate that the activity of cytosolic GSTs varies considerably in liver from various fish species from the Great Lakes. The greater GST activity in livers of bottom-dwelling fish might be interpreted as an evolutionary adaptation to provide resistance to the potentially genotoxic and carcinogenic effects of xenobiotic compounds, that are necessarily detoxified by GSTs, to which these fish are exposed in their benthic environment. This interpretation is supported by the finding that liver cytosol from benthic fish species provided greater protection against DNA binding by the carcinogenic PAH metabolite BPDE, and the reactive intermediate B[a]P-4,5-oxide. This variation in constitutive GST-mediated protection in fish might explain differences in susceptibility of various fish species to PAHs in contaminated sediments. Recent evidence from epidemiological and laboratory studies in various bottom-dwelling fish support the hypothesis that reduced GST-mediated protection might explain differences in susceptibility to some environmental carcinogens. For example, English sole *(Parophrys vetulus)* show a higher prevalence of liver cancer compared to starry flounder *(Platichthys stellatus)* from industrially polluted estuaries of Puget Sound, Washington (7,9). Studies of BaP metabolism in these fish have demonstrated that *in vivo* binding of ^{3}H-BaP to hepatic DNA is approximately twice the level in English sole compared to Starry flounder (7). HPLC analysis has revealed a much greater proportion of biliary BPDE-GSH conjugates in the bile of Starry flounder than in English sole (9) .Also, hepatic GST (CDNB) activity is three-fold higher in Starry flounder compared to English sole (7). Similarly, tumor surveys of Great Lakes fish indicate a higher frequency of liver tumors occurs in bottom-dwelling brown bullheads *(Ictalurus nebulosus)* compared to carp *(Cyprinus carpio)* collected from the same polluted areas in Lake Erie (5,11). Recent comparative studies of BaP-7,8-diol metabolism in hepatocytes isolated from brown bullheads and carp revealed that carp hepatocytes metabolized BP-7,8-diol faster than bullhead hepatocytes producing a larger proportion of GSH conjugates (34). However, higher levels of BaP-DNA adducts which occur in carp hepatocytes fail to explain higher susceptibility of brown bullhead to PAH-associated liver cancer.

In some white suckers from various sites in the Great Lakes, a parasitic obstructive hepatobiliary disease is associated with severe regional cholestasis of distal liver lobes. The nature of this segmentally obstructive liver disease provides an opportunity in which to evaluate acquired alterations in GST activity and regional differences in carcinogen metabolism in a unique natural model of inflammatory liver disease. The results of these experiments indicate that obstructive liver disease and cholestasis in white suckers reduces hepatic glutathione S-transferase activity for CDNB as a substrate. Because amounts of GST subunits were similar, this reduction appears to be due to an inhibitory effect of some substance in cholestatic liver. During cholestasis, the intracellular concentration of organic ions, such as bile acids and bile pigments, increase to levels (35,36) which can impair the catalytic activity of GSTs. Heme catabolites, namely hematin, biliverdin, and bilirubin, and also bile acids namely CDCA and DCA, inhibited CDNB conjugating activity of white sucker cytosol and purified GSTs *in vitro*. This suggests that some bile acids and bile pigments that accumulate during cholestasis may contribute to the lower activity measured.

An important issue that is addressed in this study is whether inhibition of GSTs, that is associated with bile duct obstruction and cholestasis in white suckers, alters the ability of GST isoenzymes to detoxify carcinogens such as BaP. The present experiments indicate that bilirubin is one endogenous nonsubstrate ligand capable of inhibiting cytosolic GST activity towards BaP-4,5,oxide *in vitro*. This interpretation is supported by moderate but significantly less protection against the binding of BPDE to DNA in cytosol from obstructed liver compared with adjacent unobstructed liver. However, the levels of binding of BaP metabolites to macromolecules in fish given ^{3}H-BaP *in vivo* indicate that cholestasis had negible influences on binding of ^{3}H-BaP to hepatic DNA. While this suggests that alterations in GST activities in obstructed lobes do not reduce resistance to BaP at these low doses, the possibility that altered GST functions increase sensitivity to BaP at higher doses, or to other environmental PAHs was not evaluated. Recent studies, in which DNA adducts were examined in the liver of English sole treated with variable doses of BaP, indicate that the formation of BaP-DNA adducts is linear at doses ranging from 2 to 100 µg/g suggesting that in this low dose range neither activation nor detoxification pathways are saturated (37,38). However, a possible threshold dose of PAHs for DNA adduct formation might exist at higher doses particularly in liver with compromized phase II detoxifying capabilities such as occurs in suckers with cholestasis. Also, the rate of DNA repair in sucker liver during the 24 hour period following BaP administration might be sufficient to compensate for increases in PAH-induced DNA damage. Thus, the hypothesis that reduced GST-mediated protection predisposes to PAH-induced genotoxicity in white suckers remains unsupported but also unrefuted. However, the results of these studies suggest that BaP is not an important carcinogenic PAH in white suckers, even if their livers are obstructed. Accordingly, other environmental contaminants, including other important PAHs, might be more important than B[a]P in the pathogenesis of liver cancer in white suckers. These findings suggest that chemicals most likely to be involved will be much more genotoxic when hepatic GSTs from white suckers are inhibited. Our assays used in these studies provide a means of making this determination on candidate environmental carcinogens.

The presence of parasites and parasitic lesions in fish with segmentally obstructive liver suggests that parasitism may be directly involved in the pathogenesis of obstructive bile duct disease. The chronic inflammatory bile duct disease is widespread in white suckers in the Great Lakes and not consistently associated with hepatic neoplasms which are found preferentially in industrially polluted locations. This suggests that parasitic liver disease is not exclusively responsible for neoplastic development, but it cannot be dissociated from the neoplastic disease because the parasitic disease is endemic in all sites examined. Thus the disease might be an important influencing factor in the pathogenesis of liver neoplasia in these fish. Concurrent nonneoplastic liver lesions, including inflammatory, degenerative and necrotic lesions, and neoplastic hepatic lesions have also been observed in other studies of pollution-associated neoplasia in both marine and freshwater bottom-dwelling fish (2,6,8,10,14). Myxosporeans (2) and bile duct inflammatory disease with cholestasis has been observed in English sole from Puget Sound (2,39), suggesting a similar association of liver disease and neoplasms as we have observed in white suckers in Lake Ontario. While it is not possible to determine, from the present study alone, the role of parasitic disease in the development of liver neoplasms in white suckers from polluted environments, there is substantial epidemiological evidence supporting a correlation between liver cancers and inflammatory liver disease in humans infected by Hepatitis B virus or various parasites (15,16). However, the cellular and molecular mechanisms underlying this association are unclear. Increased proliferation of bile duct epithelium observed in white suckers with cholangiohepatitis and cholangiofibrosis might be an important contributor to the co-occurrence of liver neoplasia and bile duct disease in white suckers. However, chronic inflammation and liver cell injury might also increase susceptibility to liver carcinogens by altering activation, detoxification or biliary excretion of carcinogens, or altering DNA repair mechanisms (20,21). The reduction in GST activity, in association with inflammatory bile duct disease and cholestasis, might represent another mechanistic explanation that does not exclude the possibility that the increased rate of proliferation and other influences may also be involved. The results of this study do suggest that while bottom-feeding white suckers are remarkably resistant to BaP, parasite-associated bile duct disease could interfere with detoxification of other xenobiotics detoxified by GSTs.

Because of the complexity and multifactorial nature of pollution-associated hepatocarcinogenesis in bottom-dwelling fish, the relevance of this problem as an indicator of the status of their aquatic environment is not easily established. The use of tumor surveys in wild fish, without supportive data from mechanistic studies, might lead to the erroneous interpretation of epidemiological studies or implementation of ineffective or irrelevant remedial action. For example, if the parasite burdens decline, it might be reflected in fewer tumors even if carcinogen contamination is increasing. By investigating factors which influence the development of liver cancer in various fish and mammalian models of hepatocarcinogenesis, the judgement of potential risk of cancer development in humans might be made with greater confidence. For example, variations in constitutive resistance to carcinogens between various species of fish, and between individuals in human populations, suggests that the risk of developing cancer is not uniform in heterogenous populations. Questions such as "are humans similarly sensitive to environmental carcinogen X, as rats, or mice, or white suckers or some other species?" are important in the context of how risk assessment is currently performed. However, recognition of constitutive differences within and among species in the expression and function of resistance systems, or acquired differences associated with concurrent disease, preneoplasia, or exposure to competitive inhibitory or inducing substances, presents a complex situation that cannot be handled optimally with simple regulatory rules based on simple assumptions. Furthermore, interactions between various environmental, endogenous, therapeutic or nutritional substances in the pathways involved in biotransformation and detoxification might increase the sensitivity of individuals to carcinogens to which they are normally resistant. One ultimate challenge is to increase our understanding of the complex carcinogenic process and to more reliably predict and estimate cancer risk in human populations. This objective is somewhat separable from objectives for ecosystem maintenace and remedial action. Recognition of the obstacles in the way of these various objectives, and the limitations in approaches based on simpler notions of carcinogens as health hazards or environmental impacts is an important stage in this pursuit.

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Table 1. *Inhibition of white sucker hepatic GSTs by various endogenous nonsubstrate ligands*

Inhibitor	I_{50} (µM) Cytosol	I_{50} (µM) Affinity Purified GST
DCA	240.0	267.0
CDCA	75.0	115.0
Bilirubin	N.D.	18.8
Biliverdin	12.5	6.3
Hematin	0.6	0.4

The I_{50} value is the concentration of inhibitor giving 50% inhibition of the enzyme activity at pH 7.5 with 0.5 mM CDNB as a substrate in the presence of 2 mM GSH. The inhibition studies were performed by preincubating the enzyme with inhibitor for 5 minutes at 25°C prior to the addition of substrates. Experimental details are outlined under Methods. The specific activities (µmol CDNB/min/mg protein) of the GST enzymes were: cytosolic GST, 0.75 ±0.06; affinity purified GST, 6.9 ±1.1. Values represent the means of three determinations which were within 5%. N.D. (not determined), bilirubin failed to reduce the cytosolic GST activity by 50% at the highest concentration assayed (100 µM).

Table2. *Differences in cytosolic GST activity, cytosolic GST-mediated protection against BPDE-DNA binding in vitro and BaP-macromolecular binding in vivo in obstructed and surrounding liver in White suckers*

	Liver Region			
	N	Obstructed	N	Surrounding
GST activity (CDNB)[a]	6	0.25 ±0.08[e]	6	0.55±0.08
BaP-macromolecular binding				
In vitro				
BPDE-DNA	6	20.6 ±1.6	6	16.4 ±1.3
In vivo[d]				
BaP-protein	4	7.6 ±3.0[f]	4	4.6 ±1.9
BaP-DNA	4	0.24 ±0.1	4	0.25 ±0.2

[a] Values expressed as µmoles CDNB/min/mg protein represent the mean ±SE of 3 determinations.

[c] Values, expressed as pmoles ^{3}H-BPDE bound/mg DNA/8 min. ^{3}H-BPDE was incubated in the presence of 0.2 mg calf thymus DNA, NADPH (2mM), GSH (2.5 mM) and 1.6 mg cytosolic protein (from obstructed or surrounding liver). Values represent the mean ±SE of two determinations.

[d] Values are expressed as fmoles BaP bound/mg protein or DNA and represent the mean ± SE of 4 determinations. Suckers, with obstructions visible on laparotomy, were orally administered 5 µCi ^{3}H-BaP (56 Ci/mmol). Livers were sampled at 24h, DNA and protein were isolated and quantified and BaP-derived radioactivity was measured by liquid scintillation counting.

[e] Statistically different from cytosol from surrounding liver ($p \leq 0.05$)

[f] Statistically different from protein adducts in surrounding liver ($p \leq 0.05$)

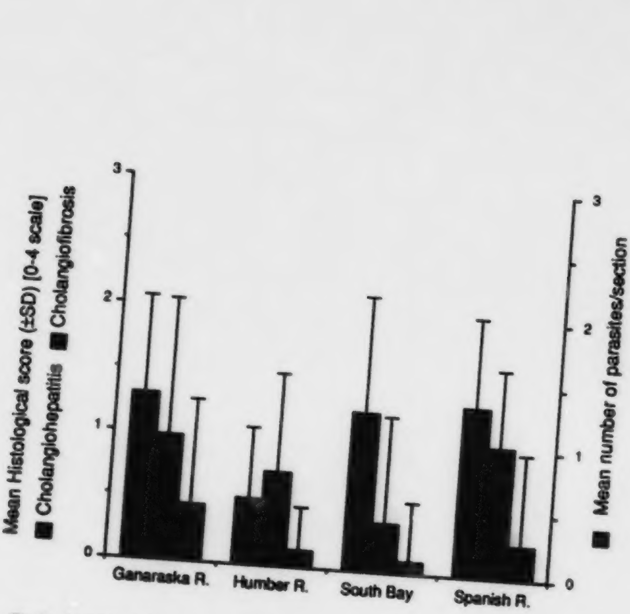


Fig.1. Severity of lesions and numbers of parasites in inflammatory liver disease in white suckers from various sites in the Great Lakes. Histological sections (5μm) of liver from white suckers from Lake Ontario (Humber R., N=46 and Ganaraska R., n=40) and Lake Huron (South Bay, Lake Huron, N=47 and Spanish R., N=46) in the Great Lakes were stained with H&E and were examined for the presence of inflammatory lesions of cholangiohepatitis or cholangiofibrosis. Lesions were graded on a scale of 0 to 4 (0: no visible lesions; 1: mild; 2: moderate; 3: marked; 4: severe) and the number of parasites visible per section was also noted. Because parasites were rarely encountered, the numbers collectively represent flukes *(Diginea: Sanguinicola)*, nematodes *(Spirurida: Acuarioidea)*, and protozoa *(Myxozoa: Myxosporea)*, all of which were present in some fish from all sites.

Figure 2. Hepatic Cytosolic Glutathione S-transferase Activity in Various Fish Species

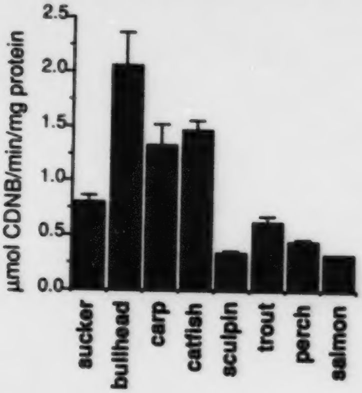
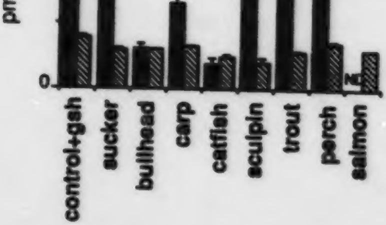


Figure 3: DNA Binding by B[a]P-7,8-diol-9,10-epoxide (BPDE) and B[a]P-4,5-oxide in the Presence of GSH and Dialysed Liver Cytosol from Various Fish Species



THE SIGNIFICANCE OF METABOLIC CHANGES IN EASTERN WHITE PINE SEEDLINGS FOR EARLY DIAGNOSIS OF FLUORIDE INJURY.

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ABSTRACT

Eastern white pine (Pinus strobus L.) seedlings were treated with 0.5, 1 and 2 ppb hydrogen fluoride for 1, 7 and 30 days and seedling water relations, plasma membrane structure and cell ultrastructure were studied to detect early metabolic changes leading to needle injury. First visible signs of fluoride injury appeared on needles after 20 days in 0.5 ppb, 9 days in 1 ppb and 5 days in 2 ppb treatments. Hydrogen fluoride reduced seedling transpiration rates after only 1 day of treatment with all three fluoride levels. At that time tissue fluoride concentrations were similar to those in control plants. Reduced transpiration rates resulted in higher (less negative) water potentials and seedling water contents. However, despite high water potentials membrane leakiness was observed in plants treated with 2 ppb fluoride for 1 day. Plasma membranes isolated from fluoride treated plants showed a number of alterations in chemical composition compared with control seedlings including changes in sterol content and ATPase activity. Few ultrastructure changes could be observed on the electron microscopy level. The results of this study strongly implicate plasma membrane in the development of fluoride injury.

INTRODUCTION

Fluoride is a common environmental pollutant released during various industrial processes. However, the assessment of vegetation damage caused by fluoride is difficult. Visible and metabolic fluoride injury symptoms are often easily confused with the symptoms occurring as a result of drought and other environmental conditions as well as the pathogens. Secondly, vegetation damage can occur in the absence of visible fluoride injury (Treshow et al. 1967, MacLean et al. 1977). Measurements of fluoride tissue levels also poorly reflect fluoride damage because effects on metabolic processes and cell structure could exist before measurable fluoride accumulation.

The present study investigated the effects of low doses of hydrogen fluoride treatment on water relations and plasma membrane structure and composition in needles of eastern white pine seedlings. The main objective of this study was to examine the significance of metabolic changes in plants exposed to hydrogen fluoride for early detection of fluoride injury.

MATERIALS AND METHODS

Experimental conditions

Nine-week-old eastern white pine seedlings were treated with hydrogen fluoride in plexiglass fumigation chambers which were placed in controlled environment growth cabinets. Fluoride treatments included 0.5, 1.0, and 2.0 ppb hydrogen fluoride for 1, 2, 7, 8, and 29 days. The following conditions were maintained in the fumigation chambers during the experiments: day/night temperatures, 22/15°C; relative humidity, 88%; 18-h photoperiod.

Measurements of water relations, membrane leakiness and fluoride content

Transpiration rates were measured inside the growth chambers using LI-1600 (Li-Cor, Lincoln, Nebrasca, U.S.A) steady state porometer (n=8).

Water potentials were measured in shoots (n=8) using a pressure chamber technique (Scholander et al. 1965).

Water content (n=8) was estimated by weighing needles before and after drying them in an oven at 85°C for 24 hours.

Fluoride content (n=4) was measured using an alkali fusion -selective ion electrode technique of McQuaker and Gurney (1977).

Electrolyte leakage from needles was determined by measuring electrical conductance of a cell effusate as described by Zwiazek and Shay (1988). Needles (7 needles per sample, n=5) were briefly washed, placed in test tubes containing deionized water, cut into segments and incubated at 21°C. After 1 h, the solutions were replaced with 5 ml of fresh deionized water and the incubation continued for 5 h. Electrical conductance of the effusates was measured with Mdl C33 conductivity meter (Fisher). After the measurements, the needles were frozen and stored overnight in a freezer at -15°C. The following day the needles were again incubated for 5 h and the electrical conductances of cell effusates were measured to determine the total needle electrolyte content.

Plasma membrane isolation

Fresh needles (20 g) were homogenized with 100 ml of the extraction medium containing 1% PVP and 0.16 ml mercaptoethanol in 0.75 M Tris-acetate buffer at pH 7.0. The homogenate was filtered through 4 layers of cheesecloth, and centrifuged at 600 g for 15 min. The pellet was discarded and the supernatant was centrifuged at 70 000 g for 1

h. The pellet obtained as a result of this centrifugation was resuspended in 5 ml of a medium containing 0.5 M sucrose and 10 mM sodium phosphate (pH 7.8) and used for phase partitioning against 3350 polyethylene glycol and dextran 500. Phase partitioning was carried out according to Hellergren et al.(1983).

Plasma membrane lipid analysis

Lipids from the plasma membranes were extracted with acetone:ethanol (1:1, v:v) followed by chloroform:methanol (2:1, v:v) and chloroform. All solvents were evaporated and lipids resuspended in a small volume of chloroform and applied to a silicic acid column (0.5 x 5 cm, 100-200 mesh, Sigma Chemical Co., St. Louis, MO, U.S.A.). The lipids were separated into different polarity classes by washing the column with 10 column volumes of chloroform, followed by 40 volumes of acetone, 10 volumes of chloroform:methanol (1:1, v:v) and 10 volumes of methanol. The chloroform fraction contained sterols, the acetone fraction contained mostly galactolipids, and the chloroform:methanol and methanol fractions contained phospholipids.

For sterol analysis, internal standard (cholestane) was added to the chloroform fraction and chloroform was evaporated under nitrogen. Sterols were dissolved in 0.5 ml pyridine and derivatized by adding 0.1 ml trimethylchlorosilane followed by 0.2 ml hexamethyldisilazane. Derivatized samples were injected into a Hewlett Packard 5890 gas chromatograph equipped with a 30-m-long, 0.25-mm internal diameter DB-5 column (J&W Scientific Folsom, CA, U.S.A. Conditions of the analyses were: carrier gas (helium) flow, 20 ml min^{-1}; oven temperature, 285°C; detector and injector temperatures 300°C. Sterols were identified by cochromatography with standards obtained from Sigma and on the basis of their mass spectra after GC-MS analysis of the samples.

The fractions containing phospholipids and known amounts of internal standard (phosphatidylcholine diheptadecanoyl) were combined, the solvents were evaporated under nitrogen and phospholipids suspended in 0.5 ml chloroform. Fatty acids of the phospholipids were transestrified prepared using 0.5 M sodium methoxide. Fatty acid methyl esters were analyzed using a Hevlett Packard 5890 gas chromatograph equipped with a 30-m long, 0.25-mm internal diameter DB-225 column. Conditions of the analyses were: carrier gas (helium) flow, 15 ml min^{-1}; oven temperature, 200°C; detector and injector temperatures 250°C. The identification of phospholipids was confirmed by cochromatography with authentic standards.

Measurements of plasma membrane ATPase activity

ATPase activity was determined in a reaction medium consisting of 10-20 µg membrane protein, 3 mM ATP, 4 mM $MgSO_4$, 50 mM KNO_3, 1 mM sodium azide, 0.1 mM sodium molybdate, 50 mM MES-Tris (pH 6.5), 0.25 M sucrose, 0.1 mM EDTA, 1 mM DTT, 0.05% Triton X-100, and 0.5 mM orthovanadate. Orthovanadate was stored as 5 mM vanadate solution and prepared by dissolving V_2O_5 in 20 µM NaOH at pH 11.8 (Gallagher and Leonard 1982). The reaction was carried out at 38°C and stopped after 30 min by addition 1 ml ascorbate/molybdate solution [3% (w/v) ascorbic acid, 1% (w/v) sodium dodecyl sulfate (SDS), 0.5 M HCl mixed 15 min before use with freshly made 8% (w/v) ammonium heptamolybdate in a ratio of 10:1)]. Released inorganic phosphorus (P_i) was estimated using the method described by Widell and Larsson (1990). In addition, the inhibitors of acid phosphatase (0.1 mM sodium molybdate), mitochondrial and chloroplast ATPase (1 mM sodium azide), vacuolar ATPase (25 mM $NaNO_3$) and plasma membrane ATPase (50 mM sodium vanadate) were added as required in order to determine the purity of the plasma membrane fraction and inhibit non-plasma membrane ATPases. The protein content of the plasma membranes was estimated by a modified micro-Lowry method (Peterson 1977) using bovine serum albumin as a standard.

RESULTS

Fluoride content and water relations

Hydrogen fluoride fumigation with 0.5, 1.0, and 2.0 ppb resulted in an increase of tissue fluoride content after 7 and 23 days. After 2 days fluoride content was similar to those in control plants (Fig.1a). First visible signs of fluoride injury appeared on needles of some seedlings after 20 days in 0.5 ppb, 9 days in 1.0 ppb and 5 days in 2.0 ppb treatments.

Low (0.5 ppb) and high (2 ppb) hydrogen fluoride levels resulted in a decrease in seedling transpiration rates after only 1 day of treatment (Fig.1b).

Water potentials in fluoride treated seedlings remained higher (less negative) than those in control seedlings after 7 and 29 days (Fig.1c)

Water content increased as a result of fluoride fumigation. This was particularly noticeable after 7 and 29 days in plants treated with 0.5 ppb and 1.0 ppb fluoride.

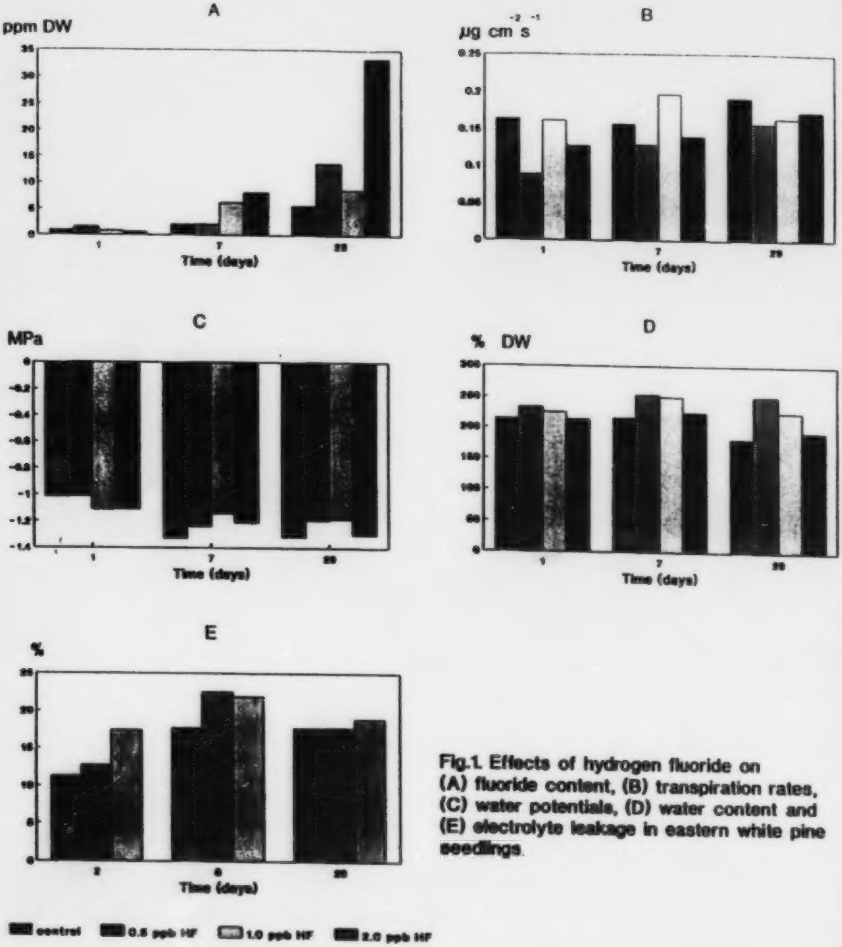

Fig.1. Effects of hydrogen fluoride on (A) fluoride content, (B) transpiration rates, (C) water potentials, (D) water content and (E) electrolyte leakage in eastern white pine seedlings.

Table 1. Effect of hydrogen fluoride on lipid composition in plasma membranes from eastern white pine needles (two-day exposure)

Treatment	Sterols [µg mg Protein^{-1}]	Phospholipids [µg mg Protein^{-1}]	Sterols/Phospholipids [weight ratio]
Control	39	50	0.78
0.5 ppb	183	50	3.66
2.0 ppb	150	42	3.75

Effect of fluoride on membrane function and composition

Hydrogen fluoride treatment resulted in an increased release of electrolytes (Fig.1e). After 2 days in 2.0 ppb treated plants electrolyte leakage was about 50% higher compared with control. After 8 days electrolyte leakage was also higher in 0.5 and 2.0 ppb treated plants. Almost full recovery was observed in plants treated for 29 days (Fig.1e).

HF fumigation for 2 days increased the content of sterols and had little effect on the content of phospholipids in the plasma membranes of plants treated with 0.5 and 2.0 ppb levels (Table 1). This resulted in higher sterols/phospholipids ratios in HF treated plants.

Plasma membrane ATPase activity was strongly inhibited by 0.5 and 2.0 ppb treatments and it measured 31.1 and 8.0 nm P mg^{-1} protein min^{-1} in plants treated for 29 days compared with 99.3 nm P mg^{-1} protein min^{-1} in control seedlings.

Electron microscopy

For electron microscopy needles of plants without visible signs of injury (treated with 0.5, 1.0 and 2.0 ppb fluoride levels after 1, 7 and 30 days of HF fumigation) were used. There were no detectable changes in the ultrastructure of mesophyll cells which could be attributed to fluoride.

DISCUSSION

Fluoride affects plants at the metabolic level even in the absence of visible injuries (Treshow et al. 1967; MacLean et al. 1977). In this study numerous physiological and biochemical changes could be observed long before the appearance of necrotic lesions on leaves and before any ultrastructure changes could be detectable. In previous studies (Zwiazek and Shay 1987, 1988), sodium fluoride applied to the soil resulted in a severe water stress in jack pine seedlings. Therefore, on the metabolic level the effects of water stress could not be easily separated from a direct effect of fluoride. The results of the present study show that gaseous hydrogen fluoride did not cause water stress in eastern white pine seedlings. An early effect of fluoride was seen as stomatal closure an drastic inhibition of transpiration rates in those seedlings which had tissue fluoride levels similar to control plants. Another early effect of fluoride was an increase in membrane permeability measured as electrolyte leakage. The analysis of plasma membranes showed a drastic increase in sterol to phospholipid ratios in fluoride treated plants. This increase may constitute an important factor affecting membrane ATPase activity and result in membrane leakiness. Plasma membrane composition and ATPase activity may be useful in determining early fluoride effects on plants. Future studies will examine the ability of plants to recover after fluoride treatments and restore normal metabolic activity.

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Interactions of Polycyclic Aromatic Hydrocarbons with Higher Plants: Photoinduced Toxicity and Development of a Phytotoxicity Assay

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Key words: PAH, phytotoxicology, duck weed, UV_B, ozone depletion, photoinduced toxicity.

Summary Polycyclic aromatic hydrocarbons (PAHs) are a prevalent group of toxic and mutagenic environmental contaminants. Light increases PAH impacts through photosensitization reactions (e.g. generation of singlet oxygen) and, as we have found, by oxidation of the chemicals. To examine the modes of PAH action in solar radiation and the degree of involvement of the photomodified compounds, the photoinduced toxicity of six representative PAHs (anthracene, phenanthrene, benzo(a)pyrene, fluoranthene, pyrene and naphthalene) to the aquatic higher plant *Lemna gibba* L. G-3 is being investigated. Toxicity endpoints were inhibition of growth, chlorosis and photosynthesis. The UV portion of solar radiation was most active at inducing toxicity. The toxicity of all six chemicals was dependent both on chemical dose and light intensity. To specifically explore whether photomodified PAHs contribute to toxic action, the chemicals were irradiated prior to application to the plants. The rates of photooxidation of the six PAHs were rapid on an environmental time scale and the relative velocities for four of the chemicals were coincident with their order of toxic strength. Strikingly, all the PAH photoproducts were much more toxic to *Lemna* than the parent compounds. It is thus apparent that photooxidized PAHs are of environmental concern. Since current environmental loads of PAHs are based entirely on the intact chemicals, the severity of the PAH impacts are very likely to be underestimated. In general, our research shows that the impact of light must be considered in cases where a given pollutant absorbs solar radiation.

Introduction Polycyclic aromatic hydrocarbons (PAHs), compounds consisting of two or more fused benzene rings, are ubiquitously detected throughout the environment (1-3). They are contaminants of concern in aquatic ecosystems around many industrialized areas (4-7). Being lipophilic (2, 3), PAHs readily accumulate in living organisms.

PAHs are prone to structural transformation, generally via oxidation to quinones, diols and epoxides (2, 7, 8). These reactions occur both biotically (e.g. cytochrome P450 mediated monooxygenation) (9-11) or abiotically (e.g. photooxidation) (8, 12-14). Although intact PAHs are known to be toxic and mutagenic, the risks of the chemicals are intensified if they have been altered at the structural level (1, 2, 8-11, 14). A considerable amount of research has focused on the hazards of PAHs oxidized by cytochrome P450 (9-11), however much less work has been performed on light activation of PAHs. While it has been shown that light increases PAH toxicity when the light and the chemicals are present simultaneously (14-17), the toxicity of photooxidized PAHs per se is relatively unexplored. Since PAHs are prone to rapid photooxidation (7, 8, 12-14), the modified compounds, if toxic, will contribute significantly to environmental hazards.

We have been examining how PAHs affect plants in solar radiation with a direction towards elucidating the activity of the photooxidized compounds. In this report, a summary of our work on the photoinduced phytotoxicity of anthracene (A), benzo(a)pyrene (B), phenanthrene (P), fluoranthene (F), pyrene (Py) and naphthalene (N) is provided. It is shown that environmentally relevant levels of PAHs are toxic to the aquatic higher plant *Lemna gibba* in the presence of actinic irradiation (see also 14, 20, 20a). Furthermore, the photooxidized PAHs are more toxic to plants than the intact chemicals.

Toxicity intact PAHs to plants A, P and B were selected for the first series of in-depth phytotoxicity testing because, respectively, they show high, medium and low levels of photoinduced toxic activity towards plants in simulated solar radiation (SSR, a visible:UV_A:UV_B ratio of 100:10:1) (Table 1). A and P displayed typical log-linear responses for chemical dose versus inhibition of growth (20a). The threshold of impact for A was 0.2 $\mu g\ ml^{-1}$, and acute toxicity was detected at 1 $\mu g\ ml^{-1}$, while P began to show chronic effects at 0.5 $\mu g\ ml^{-1}$ and acute toxicity at 3 $\mu g\ ml^{-1}$. Conversely, B only slightly inhibited plant growth, even at very high concentrations (4-8 $\mu g\ ml^{-1}$). We conclude that both chemical concentration and structure play important roles in PAH photoinduced toxicity to plants. Interestingly, B is highly phototoxic to animals, while P is relatively inert (15, 16). Therefore, plants and animals have divergent responses to various PAHs in the presence of actinic radiation, showing that care must be used with cross species generalizations.

Table 1

Compilation of some phytotoxicity properties of PAHs.

Chemical[1]	Toxicity[2] in SSR	Toxicity[2] with increased UV_B[3]	Rate of photoox.[4]	Toxicity[2] of photoox. PAHs	Inhibition of photosynthesis[5]
A	75	100	2 h	100	75
B	5	25	40 h	100	25
P	30	75	7 h	95	15
F	25	n.d.	>50 h	>80	25
Py	20	n.d.	15 h	>80	25
N	0	n.d.	5 h	>80	50

Data for A, B and P is from ref. 20a.

[1] Chemicals were placed in the growth medium at 2 $\mu g\ ml^{-1}$.

[2] Inhibition of growth in simulated solar radiation (SSR) at a total fluence rate of 40 $\mu mol\ m^{-2}\ s^{-1}$.

[3] UV_B content of the SSR source was elevated to 4% of the visible light intensity.

[4] Half-lives of the chemicals in 25 $\mu mol\ m^{-2}\ s^{-1}$ of UV_B irradiation.

[5] Percent inhibition of photosynthesis after incubation of the plants with the chemicals for 2 d in SSR.

The phytotoxicity of N, Py and F in SSR was also investigated. They were chosen because N is the smallest PAH, Py has a 4 ring structure and fluoranthene contains a 5 carbon ring. Py and F were found to have low levels of toxicity compared to A and P, while intact N had almost no photoinduced toxicity towards *Lemna* (Table 1). We point out, however, that N is the most volatile of the PAHs and could be depleted from the media rather rapidly. We are currently performing experiments to control for this problem. At this stage of our progress, the order of photoinduced phytotoxicity for the six PAHs in intact form is A > P > Py > F > B > N.

Effects of light quantity and quality on PAH toxicity Since light increases PAH phytotoxicity, it is important to determine if irradiation elevates toxicity in a dose dependent manner and which regions of the spectrum are most influential in the process. When the SSR fluence rate was increased from 20 μmol m^{-2} s^{-1} to 60 μmol m^{-2} s^{-1}, the toxicity of A, B and P to *Lemna* rose in proportion to intensity (20a). Note, 60 μmol m^{-2} s^{-1} is less than 5% of full sunlight (21), so there is more than enough light in the environment to activate PAHs. At 60 μmol m^{-2} s^{-1} of visible light (see below), plant growth was unaffected by any of the chemicals. This indicates that the UV component of solar radiation plays a key role in photoinduced toxicity of PAHs.

Since UV strongly influences PAH phytotoxicity, it was important to assess how an increase in UV$_B$ (the region of the spectrum attenuated by the stratospheric ozone layer [18, 21]) specifically affects toxicity. The UV$_B$ fluence rate in the SSR source was raised from 1% to 2% and to 4% of visible light while holding the levels of UV$_A$ and visible constant (this represents up to a 30 % loss of the stratospheric ozone layer). The impacts of A, P and B were enhanced by the increased UV$_B$ content (Table 1). Thus, as loss of the ozone layer continues (18), the effects of UV$_B$ on PAH toxicity could become more prevalent.

Although visible light does not activate PAH phytotoxicity at low fluence rates, at higher intensities it can induce the toxicity of A and B to *Lemna* (20a). The impacts were proportional to the light intensity. The phytotoxicity of P was not influenced by the intensities of visible light tested. This has interesting implications because P does not absorb UV$_A$ or visible light, while A and B weakly absorb in the short wavelength visible range. Thus, as the visible light intensity was raised the toxicity of A and B became more apparent. So, UV irradiation is not strict requirement for phytotoxicity, but it appears that photon absorbance by the chemical is necessary.

Photomodification of PAHs The photoinduced toxicity of PAHs is probably derived from a combination of two factors. PAHs are photosensitizers (15, 16), and in this capacity they might generate damaging singlet oxygen (19). Secondly, the compounds are prone to photooxidation (7, 13) and oxygenated PAHs (e.g. generated by cytochrome P450) are more toxic than the intact chemicals (2, 9-11). However, the toxic action of photomodified PAHs specifically is largely unexplored.

To determine if A, P and B are photooxidized rapidly enough to explain some of their phytotoxicity, the kinetics of chemical degradation in UV$_B$ and SSR were measured. It was found that under 25 μmol m^{-2} s^{-1} of UV$_B$, the half-lives of the three PAHs were very short on an environmental time scale (2, 7 and 40 h for A, P and B, respectively) (Table 1). When SSR was used to induce photooxidation, the rates of the degradation of the chemicals were slower due to the lower UV intensity, but were nonetheless fast (half-lives of 5, 20, and 72 h for A, P and B, respectively). The order of toxic strength (A > P > B) correlates with the relative rates of photooxidation, showing that photooxidation might be one of the rate limiting factors in PAH activity.

To determine if F, Py and N were also photomodified quickly enough to explain some of their toxic activity, they were exposed to UV_B for various time periods. Indeed, the three chemicals were rapidly degraded in UV radiation, showing this property is a very common trait for PAHs. Interestingly, the rates of photooxidation of F and Py are slower than A and P and are they are also less toxic, consistent with our hypothesis that the photooxidation rate of the chemicals is one of the factors controlling their phytotoxicity. We are currently testing the toxicity of photooxidized F, Py and N.

Toxicity of photomodified PAHs to plants Since the photomodification rates of A, P and B were coincident with the toxic strength of the chemicals, one could assume that the chemicals were activated upon photomodification. It was thus important to assess the toxic impacts of the photooxidized PAHs specifically. As a first step towards this end, PAHs were treated with actinic radiation for periods that assured extensive photomodification (<15% parent compound remaining). In visible light, chronic effects (growth inhibition) for the chemicals were observed at 0.2 $\mu g\ ml^{-1}$ and acute levels at around 2 $\mu g\ ml^{-1}$ (20a). Thus, photomodification of PAHs renders all three compounds to a highly toxic state in visible light. It is noteworthy that photooxidized A and P do not absorb visible light, so they are in a form that no longer requires actinic radiation for acute phytotoxicity.

The altered chemicals were more toxic in SSR than they were in visible light. The threshold for growth inhibition of the plants was very low (0.05 to 0.1 $\mu g\ ml^{-1}$) (20a) and acute toxicity was observed at 1 to 2 $\mu g\ ml^{-1}$ (Table 1). In both visible light and SSR, oxidized B, which had little toxic activity prior to photomodification, reached a level of impact similar to modified A and P. This shows that a significant portion of the phytotoxic action of B can be attributed to the photooxidized chemicals. It is clear that the altered chemicals are more phytotoxic (with or without actinic radiation) than the parent compounds were in actinic light. This is reminiscent of the increase in PAH toxicity and mutagenicity that is caused by cytochrome P450 oxidation (9-11). So, what has been assumed to be a possible PAH removal process (photodegradation) (3), may in fact be an activating mechanism.

The data also indicated that photosensitization reactions also contribute to photoinduced phytotoxicity. For example, intact F is more toxic than intact B. Yet B has a faster rate of photooxidation than F. Therefore, the toxicity of F cannot be due only to the photooxidized form of the chemical. Interestingly, F has an extremely long triplet state lifetime (1 sec), while B only has a 0.1 s triplet state lifetime (15, 16). Thus, F has the potential to be a better photosensitizer than B (more time to react with oxygen), which may explain its higher level of toxicity when applied in intact form.

The levels of impacts of PAHs in SSR show that they are very strong phytotoxicants. For example, the concentrations of photooxidized PAHs required for considerable growth inhibition (0.1 to 1 $\mu g\ ml^{-1}$ or about 0.5 to 5 μM) are on par with the effective dose ranges of many herbicides (see refs. 26, 27). Moreover, the effective concentrations of PAHs are relevant to their loads in the environment. The levels in aquatic environments around many industrialized environments range from 0.01 to 0.5 $\mu g\ ml^{-1}$ (4-7). It must be emphasized, however, that environmental PAH loads are based solely on the intact chemicals, and it is the PAHs with the slowest photooxidation rates that are detected most commonly in the environment (cf. 4, 5, 7, 13, 22-25). Furthermore, the low solubility of PAHs in water and their tendency to partition into the sediment has brought the impacts of PAHs in aquatic environments into question. However, photooxidized PAHs are more water soluble than the parent compounds. Additionally, as the solubilized PAHs are consumed photochemically, the sediment/water equilibrium will be disturbed, allowing release of the bound chemicals. While this may not be a fast process, environmental time scales are quite long. Thus, the loads and impacts of photomodified PAHs in the environment could be quite important.

Effects of PAHs on Photosynthesis A common mode of action of phytotoxicants and herbicides is inhibition of photosynthesis (27). PAHs are no exception, as derivatives of anthraquinone (oxidized anthracene) have been shown to inhibit photosystem II (28). We tested the six PAHs under study for their ability to inhibit photosynthesis. When they were applied in intact form to the plants, significant inhibition of photosynthesis (50 to 75 %) was observed for A and N (Table 1). Possibly, they inhibited photosynthesis after they have been photooxidized into the quinone species. Derivatives of anthraquinone and naphthaquinone could be site specific analogues for plastoquinone; the terminal electron acceptor of photosystem II.

We have also tested the photooxidized PAHs for their ability to inhibit photosynthesis. In this case the photo-derivatives of A and P caused severe and immediate inhibition (75 to 100 %), with oxidized N and F showing lower levels of impact (25 % inhibition). Thus, one does observe that some PAHs (probably in photooxidized form) can affect photosynthesis, pointing to one mechanism of action. However, it is not the only mechanism of phytotoxicity, as photooxidized B interrupts plant growth without major effects on photosynthesis. Thus, the photosynthesis assay not only provides a rapid assay for certain PAHs, but provides some insight into the toxicity mechanism.

Conclusions We have found that PAHs are toxic to plants in SSR and UV radiation is the key spectral region for induction of toxicity. Both chemical concentration and light intensity contribute significantly to PAH toxicity. The rate of photooxidation of the chemicals is fast enough to account for a large fraction of their toxicity, and correlations between the rate of photooxidation and toxic strength can be made. Moreover, photooxidized PAHs are more toxic to plants than the parent compounds. Thus, it is clear that the photodegradation products of PAHs should be included in environmental load surveys if we are to have an accurate assessment of the threat these compounds pose to the environment.

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MUTATIONS DETECTED IN LUNG FIBROBLASTS

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INTRODUCTION

It is now possible to detect and quantify the induction of mutations and chromosomal aberrations in lung fibroblasts of some experimental animals. Since it is just these events that are critical in the induction of cancers, knowledge of the number and types of mutations should provide a means for assessing the long term cancer risk from exposure of people to environmental pollutants, particularly inhaled pollutants. Such long term effects are of great concern because they are difficult to quantify and to investigate epidemiologically, given the long lag and the diversity of modifying factors such as cigarette smoke and diet that may exist. It is our hypothesis that if the number and kinds of mutations that any agent produces were known, the target tissues for the carcinogen could be accurately predicted. Furthermore, under conditions in which the promoting effects and protecting effects of other environmental agents were controlled, the potency of the carcinogen should also be predictable. If, for example, it were known that the critical mutational event in small cell carcinoma is a G -> C transversion in codon 12 of the H-ras oncogene followed by the deletion of an anti-oncogene on the long arm of chromosome 5, then the potency of the carcinogen would be proportional to the product of the probabilities of these two events.

This hypothesis provides a framework for understanding the complex relationship between mutagenic and carcinogenic potency and for explaining tissue-specificity of carcinogens (in part). It does not imply that there are no other factors of importance. In particular promotion, which may involve the probability of cells dividing after having been mutated, is thought to be a distinct process involving non-genetic events. Hence in a real situation the presence or absence of promoters would influence the cancer rate induced by a given mutagenic exposure. Nevertheless, the converse should also hold: in a given environment of promoters, the cancer rate would be proportional to the rate of mutation. Hence measurements of the rate of mutation in vivo are important and, in particular, the rate of specific kinds of mutational events. It should be noted that in vitro assays which do not reflect the in vivo situation, ie., the uptake, distribution, metabolism, and excretion, are not very suitable for risk evaluation but are more qualitative in nature. The assay results described here are a step to providing quantitative risk estimates. Considerable experience with the assay is summarized, the limitations of the assay are noted, and the work now in progress to characterize the nature of the mutational events is outlined.

NATURE OF THE ASSAY

The assay we have been using we call the Concurrent Assay because both chromosomal aberrations and intragenic mutations are assayed in the same cells (Heddle et al., 1990). The cells chosen for this assay are the lung fibroblasts because they are among the few cells that can be assayed for somatic mutation in vivo (Dean & Senner, 1976). Chromosomal aberrations are analyzed by the micronucleus technique (cf Heddle et al., 1983 or Heddle, 1990, for review). In this method the fact that the chromosomes were broken is detected by the presence of micronuclei which arise from chromosome fragments lost during the process of cell division. The number of micronuclei is determined by both the rate of chromosome breakage and of cell division, but the latter can be eliminated from the equation by the use of a drug, cytochalasin B (Fenech & Morley, 1986). This drug permits nuclear division, and thus the formation of micronuclei, but prevents cytoplasmic division. The result is that all cells that divide in its presence become binucleate; when only binucleated cells are scored, the influence of cell division is removed. Then the frequency of micronuclei in binucleated cells is a direct measure of the frequency of chromosomal aberrations. It does not, however, distinguish amongst those aberrations that are play an important role in carcinogenesis and those that do not. This would require a metaphase analysis, which is certainly possible for these cells. Such an analysis, like the micronucleus analysis, would be conducted on cells that had been exposed in vivo, isolated, and cultured for the analysis in vitro. The fibroblasts are facultative stem cells which do not divide at an appreciable rate in vivo unless the lung has been injured.

The detection and measurement of gene mutation in these cells is also conducted in vitro after exposure in vivo. Mutants are distinguished from normal cells by the use of the drug 6-thioguanine which is metabolized to a toxic substance by a non-essential enzyme. Cells that lack this enzyme, hypoxanthine phosphoribosyl transferase, are resistant to the drug whereas normal cells metabolize the drug and are thus killed. The genetic locus (*hpt*) that codes for the enzyme is X-linked in mammals and, thus is present in only one functional copy in both males and females. Cells that are *hpt*$^-$ have a thioguanine-resistant phenotype, TG^r. When the lung fibroblasts are cloned in the presence of thioguanine, only the TG^r cells can form colonies. The frequency of such colonies is thus a measure of the frequency of *hpt*$^-$ mutants. This frequency must be corrected for the fraction of cells that can form colonies even in the absence of thioguanine, ie., for the plating efficiency of the cells which is typically 5-20% for the lung fibroblasts.

Like the micronucleus assay, the TG^r assay provides an index of the overall rate of mutation but does not discriminate between those that play a significant role in the formation of cancers in the tissue of interest and those that do not. It is possible, however, by investigating the nature of the TG^r mutations found to determine what fraction involve any particular type of mutation. The frequency of mutations of interest will be the measurement of importance for quantitative risk estimation.

RESULTS OBTAINED WITH THE ASSAY

Spontaneous Mutations. Spontaneous mutation can occur at any time during the development of the lung fibroblast population or during the expression time in culture (cf next paragraph). A mutation that arises early in development will be present in many of the lung fibroblasts whereas one that arises late or even in culture will affect only one or a few cells. If the rate of spontaneous mutation is constant during development, then half of the mutations will affect only one cell, one quarter will affect two cells, one eight will affect four cells, and so on. Occasionally an early mutation will affect many cells, an event that is referred to as a "jackpot". Such jackpots have been detected (Heddle et al., in the press). Since not all of the cells of the lung are successfully isolated and cloned, the number of mutant colonies observed does not conform perfectly to the theoretical distribution. Micronuclei are cell lethal events and so all are recent. Their distribution is more or less normal.

Expression Time. Some time and/or cell division is required before the cell expresses the mutant phenotype, ie., becomes TG^r. Some of this is probably required for the loss of pre-existing gene product (mRNA or normal protein); some may be involved in the process of converting DNA lesions into mutations, a process that may require cell division. In any case an investigation of the frequency of mutant colonies at various time in vitro (but induced by an in vivo exposure) shows that 10 days is optimal for ethyl nitroso urea (ENU). This has been adopted as the standard time. A similar investigation for micronuclei shows that four days is optimal for X-rays and ENU. This has been adopted as the standard time.

Survival of Mutations in vivo. Two investigations of the frequency of mutations recovered at various times after exposure in vivo indicate that there is little loss of X-ray-induced mutants over a one month period whereas the frequency of ENU-induced mutants declines in an exponential-like fashion over a period of three months (Khan, Heddle, and Gingerich, unpublished results). The probable explanation for this difference is that the X-ray-induced mutations were fixed soon after exposure whereas the ENU-induced mutations arose in vitro during the process of DNA synthesis from lesions induced in vivo. This has very important implications for the interpretation of assay results, as discussed later.

Gaseous Mutagens. A series of gaseous mutagens have been tested in the assay, ethylene oxide, ethylene dibromide, methylene dichloride, and PAN (Shepson, Heddle, and Gingerich, unpublished results). Clear positive results were obtained with ethylene dibromide, but not with the other agents.

DISCUSSION

The results obtained show that the concurrent assay can be used in a routine fashion, but that it has some limitations. The first limitation, which may apply to any gene mutation assay in vivo, is that jackpots of mutations do occur. In any given experiment, therefore, a high mutant frequency in treated group could arise from a spontaneous jackpot unrelated to treatment. The solution to this problem is to require biological consistency. The jackpots will arise at random: they will rarely rise in two animals within the same treatment group, in a dose-related fashion, or in repeat experiments.

The second limitation is suggested by the decline in the number of ENU-induced mutations as a function of time in vivo. The fibroblasts are not ordinarily an actively proliferating cell population in vivo so there should be little or no selection against mutant cells so no decline was expected. Indeed, none was seen for X-rays. The X-ray-induced lesions are probably short-lived lesions that do not require DNA synthesis to be mutagenic. After X-ray treatment, the lesions are quickly repaired (and thus lost to detection) or converted to mutations which survive for long periods and are thus detected at any time after exposure. In contrast, other lesions do require DNA synthesis to be mutagenic and there is little or no opportunity for them to affect this population in vivo. Only when the cells are isolated and stimulated to divide in vitro do the pre-mutagenic lesions become important and the mutation arise. Thus if a carcinogen produced pre-mutagenic lesions that were short-lived but required DNA synthesis to be mutagenic, it probably would not be detected in this assay and negative results cannot be taken as definitive for such a carcinogen could induce mutations in the actively dividing epithelial populations that are the principal sites of human cancer.

Positive results, however, provide the possibility of investigating the nature of the mutations in detail. Clearly not all mutations are significant for carcinogenesis at a particular site. It is now possible to recover the mutant colonies obtained in the Concurrent Assay and to amplify the mutated gene in vitro for sequencing. The first step is to produce cDNA from the mRNA present in the clone with reverse transcriptase. This cDNA lacks the introns present in the gene and is thus of a manageable size. The polymerase chain reaction (PCR) has been used successfully to amplify the cDNA corresponding to the *hpt* gene from a series of ENU-induced mutants. Sequencing this DNA is our next priority.

CONCLUSION

Experience with the concurrent assay shows that it is possible to quantify both chromosomal and gene mutation rates in somatic cells treated in vivo. This permits the detailed analysis, yet to be done, of the types and frequencies of the genetic changes important for carcinogenesis. Some limitations to the usefulness of the assay have been discovered, but it will undoubtedly be useful both when positive results have been obtained and as a standard against which to judge the biological relevance of other assays, specifically those involving transgenes.

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Towards a Risk Assessment of PAH: Effects of Route of Administration and Species Differences on Tumorigenic Potency and Site of Action

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1 Summary

Our group at the Ontario Ministry of the Environment is working on a multimedia risk assessment of PAH[1] and PAH-containing complex mixtures. As a part of the risk assessment, we are examining the tumorigenic effects of PAH in animals. We are extracting and reanalyzing data from published literature using standardized quantitative methods. Whenever possible, we are comparing results obtained from experiments with the same protocol. The following are some of the main conclusions:

1. The type and site of tumors depends on both the species and route of treatment

Topical and respiratory tract administration of PAH induce tumors primarily in the tissues near the application site. In contrast PAH administered orally induced effects in a number of sites distal to the site of administration. PAH induce primarily squamous cell carcinomas in most species and with most routes considered, although adenomas and adenocarcinomas were also found relatively frequently.

2. Risk due to the exposure to PAH is strongly route-dependent

The potency of PAH is affected to a considerable degree by the route by which the PAH was taken up. Route of administration also affects sites and types of tumor induced by PAH.

3. PAH are about 250 times more sensitive to the exposure via respiratory tract than via the oral route

Rodent species examined are consistently more sensitive to 3-MC administered by the respiratory route than by the oral route. This difference needs to be reflected in the risk assessments of PAH.

4. The dependence of the potency of 3-MC on rodent species and route of administration has been estimated.

This relationship can be explored in filling the data gaps, where data on a particular compound are not available for a particular species and route of administration.

5. Risk estimates for PAH based on surface area or body weight extrapolations from rodents to humans are likely to be highly unreliable.

Potencies of PAH based on rodent to rodent extrapolation (based on body weight or surface area) were significantly different from the experimentally determined potencies. Extrapolations from rodents to monkeys produced errors of many orders of magnitude. It is likely, that the estimates of PAH potency in humans based on surface area or body weight extrapolations from rodent data could lead to substantial errors.

2 Introduction

In our efforts to conduct a risk assessment of PAH and PAH-containing complex mixtures, we are examining some key assumptions. Depending on the outcome of the evaluations, the manner in which the assessment is conducted may be changed or influenced. The current report illustrates some of the issues that we have been investigating.

Ideally, risk of adverse effects due to exposure to a toxicant could be measured directly. In practice, this is rarely possible. Regulatory agencies resort to the use of the risk assessment process for deriving quantitative estimates of risk based on incomplete data sets. The risk assessment process substitutes missing information with estimates based on other existing data and expert judgement. The eventual reliability of the risk estimates depends greatly on the reliability of the expert judgements made during the risk assessment process.

In this paper, we are examining two important issues that often need to be addressed during the risk assessment process:

- route to route extrapolation
- species to species extrapolation

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[1] **Abbreviations:** PAH - Polycyclic Aromatic Hydrocarbons
3-MC - 3-methylcholanthrene
B[a]P - Benzo[a]pyrene

2.1 Route to route extrapolation

The role of the route of administration on the potency of a toxicant is often overlooked. In many cases, a toxicant is assumed to have some inherent potency, independent of the route of uptake. Furthermore, most risk assessments are conducted assuming that exposure occurs through a single medium and via a single route. In practice, that is often not the case. For example, if the exposure is from a particulate-bound toxicant in the air, the uptake will take place both in the respiratory tract and in the digestive tract. Also, humans are exposed to many toxicants from more than one medium. Therefore, it is important to understand how to estimate the risk from a toxicant which can be taken up by multiple routes.

In the case of PAH, it is especially important to understand the effect of the route of administration on the toxicity of these compounds. People are exposed to PAH primarily by ingestion and inhalation. However, in most experimental studies PAH were applied topically to the skin. Since, the risk assessment calls for extrapolation from the experiments (with topical administration) to humans (with primarily oral and respiratory uptake), it is important to understand how the route of administration affects the toxicity of PAH. We must consider the fact that humans receive greater exposure to PAH through ingestion rather than inhalation. Yet, studies for humans exposed to PAH-containing mixtures, showed greater tumorigenicity through inhalation and lower tumorigenicity through ingestion.

Both these facts, illustrate why we need a comprehensive understanding of the effects of the route of exposure (administration) on the potency of PAH, in order to conduct an accurate estimate of risk.

2.2 Species to species extrapolation

When there are inadequate data to estimate the potency of a toxicant in humans, the potency is usually extrapolated from experimental data. It is often assumed that the potency in a target species (e.g. human) is a function of a potency in the reference species (e.g. mouse) and a function of body size. The US EPA uses the assumption that the target dose is proportional to surface area, where surface area is estimated as the square of the cube root of the body weight. The FDA uses the assumption that the target dose is proportional to the body weights of the species. Many experimenters have studied the relationship between potency and body size in order to formulate a generalized relationship, which would be accurate for many species and many toxicants.

We set out to test the relationship between the species body size and potency *specifically* for PAH. Since there are no human data on the potency of individual PAH, we tested whether there is a consistent relationship between potency and body size in different experimental species. We reasoned that, if its possible to predict potency of PAH in humans from rodent data, it should be possible to extrapolate from one experimental species to another. The results of these extrapolations are reported in the *Results* section.

3 Results

3.1 Route and site of action

In general, administration of PAH tends to produce primarily squamous cell carcinomas in most species and routes considered here (See Table 3.1.1). Adenomas and adenocarcinomas are also found relatively frequently. In hamsters, skin application of PAH results in melanomas, rather than papillomas or squamous cell carcinomas.

With skin and respiratory tract application, tumors tend to form near the site of initial contact with the tissue. Thus, skin is the primary target for PAH applied topically. Thyssen *et al.* [36] conducted an experiment where tumors developed all along the respiratory path with the exception of the lungs. It is likely, that the lungs remained tumour-free because only low concentrations of B[a]P reached the lungs. Some tumors also developed in the upper digestive system, probably in response to the particles deposited there by reverse transport from the respiratory tract. When PAH are applied at a specific site of the respiratory system, the tumors develop near that site.

Unlike skin or respiratory tract administration, administration to the GI system results in tumor development at some distance from the application site. When PAH were administered orally to female rats, tumors were observed in mammary tissue but not in the GI system. Mammary tumors were also observed in mice given oral administration. In hamsters, oral administration of PAH induced skin melanomas. See Table 3.1.1.

Repeated oral administration of B[a]P to mice induced tumors in the forestomach, but lung tumors and leukemia were also observed. Interestingly, forestomach tumors are also found in mice treated with PAH intracolonically. This suggests that forestomach tumors are not induced by oral administration of PAH just because this is the first site of contact with these compounds. See Table 3.1.1.

It is important to note that there are important species differences in the site and type of tumors induced by PAH in different species. Thus, application of PAH to the skin of mice and rats produces papillomas and squamous cell carcinomas but in hamsters the predominant type of tumor is melanoma. Oral administration of PAH to female rats induces mammary tumors, while in the mouse, forestomach tumors predominate. As a result, caution is recommended when attempting to extrapolate findings in one species to another.

Table 3.1.1. **Sites and Types of Tumors Found with Different Routes of Administration.** Table 1 shows whether an organ (or organ system) is a major or minor site for tumors, the organs in which tumors have been observed and the types of tumors observed.

Route	Species	Site and Type of Tumor					Ref.
		Skin	Mammary	Respiratory	GI	Other	
Topical	Mouse	■					7, 32, 33, 34
	Rat	■					28, 39
	Hamster	▨					5, 12, 16, 31
GI	Mouse	■	■	■	■		2, 22, 25, 26, 27, 35, 37
	Rat		■			■	17-19, 29
	Hamster	▨				Liver	3, 4, 16
Respiratory Tract	Mouse			■			20, 30
	Rat			■			6, 8, 9, 14, 23
	Hamster			■			10, 11, 13, 36, 38

Legend

Squamous carcinoma
Adenoma, Adenocarcinoma

Major Site	■	▨	Other
Minor Site	■	▨	Other

Squamous carcinoma
Adenoma, Adenocarcinoma

3.2 Route of exposure and potency of PAH

Figure 3.2.1 illustrates that there is a considerable difference between the potency of 3-MC administered by different routes. In general, PAH induce tumors most readily via the respiratory route, although mice may be somewhat more sensitive to topical administration of 3-MC. Tumors were least readily induced by oral administration; specifically, hamsters showed no effect at the tested dose. Table 3.2.1 shows the relative potency of 3-MC when applied to different rodents and through different routes. All species and routes have been normalized to mouse-skin. Thus, mouse skin has a potency of one.

Table 3.2.1. Relative potency of 3-MC in rodents when administered by different routes. Potencies are determined relative to mice treated with topical application; thus, potency in mice treated topically is set to 1.0.

Route	Species			
	Mouse	Rat	Hamster	Geometric mean
Topical	set to 1	.035	*	.19
Respiratory Tract	.26	1.9	1.9	.98
Oral	.019	.0033	.0010	.004

* *No effect at tested dose*

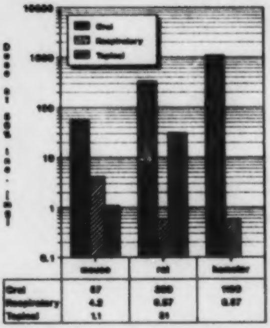


Fig 3.2.1: The dose of 3-MC required to induce 50 percent tumors in rodents. For mice and rats the least sensitive route of administration was the oral route. Hamsters showed no effect for skin application. Mice were almost equally sensitive to 3-MC applied topically or administered to the respiratory system.

3.3 Species to species extrapolations

The results in figures 3.3.1a to 3.3.1d indicate that there is a considerable difference between the dose of 3-MC which was experimentally determined to induce a particular tumor incidence in a particular species and the dose predicted based on surface area or body weight extrapolation from one species to another.

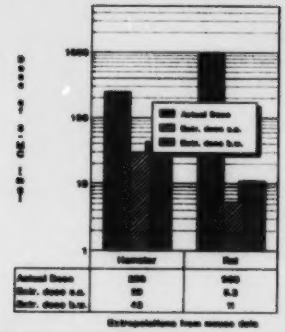
4 Discussion

4.1 Methodological issues

It was necessary to draw comparisons between species and routes of administration from the data obtained from studies originating in different laboratories. We were rarely able to make comparisons where all the experimental parameters were the same in all the studies except for the parameter being compared. We made an effort to locate the papers with as similar an experimental design as possible. In particular, we identified studies which used the same compound for testing (3-MC) and observed the same endpoint (e.g. lung squamous cell carcinoma). We have also compared, whenever possible, experiments where the exposure to 3-MC was protracted over days or weeks (sustained release material or repeated administration).

The sensitivity of different species to PAH is hard to evaluate. Some problems stem from the different life expectancy and from histological/ anatomical differences among the species. (Example: what should be considered a primate equivalent of the rodent forestomach?) Furthermore, dose-response curves are rarely available and thus, by necessity, the comparisons were often conducted on experiments with only a single dose of PAH tested.

It is also difficult to decide, whether the validation of species extrapolation should be conducted using the most sensitive endpoint or whether the same endpoints should be used for comparison. For example, there are few data on mouse mammary tumors induced by oral administration of PAH but there are good data on forestomach tumors. In contrast, much of the rat data involve mammary tumors as endpoints. Selection of endpoints affects the conclusions about the relative sensitivity of different species. The inter-species differences are more marked, when a standard endpoint is monitored. If the most sensitive endpoints are examined, then the inter-species differences are usually smaller in magnitude. Thus, rats develop respiratory system squamous cell carcinomas much more readily than mice, based on constant surface area or constant body weight extrapolations. Mice develop adenomas



Rat extrapolated at 1% incid.

Fig. 3.31a

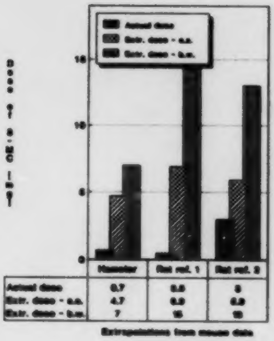
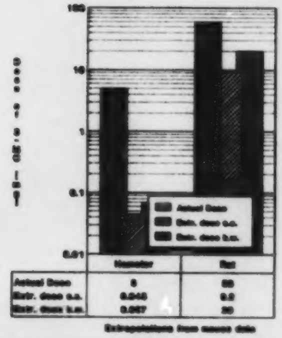
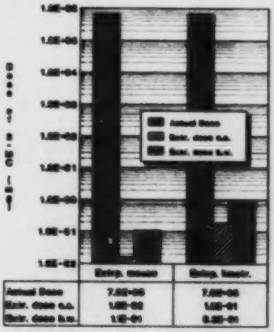


Fig. 3.3.1b



Hamster extrapolated at 1% incid.

Fig. 3.3.1c



Monkey extrapolated at 1% incidence

Fig. 3.3.1d

Fig. 3.3.1. Observed and extrapolated potency of 3-MC in experimental species. a) Oral administration in rodents. b) Respiratory administration in rodents. c) Topical administration in rodents. d) Subcutaneous administration in monkeys. Extrapolations were done from a reference species (mice in a, b, c, d, and hamsters in d) using both surface area and body weight. In a) Mice and hamsters developed forestomach tumors but rats did not; however, rats developed a high incidence of breast adenocarcinomas (50-70%). The observed rat incidence was set to one percent gastric tumors for the purpose of the second stage of the extrapolation. The dose predicted by both extrapolations was lower than the actual dose required i.e. the extrapolations indicate that 3-MC is more potent than experimental observations show it to be. In b) All species produced squamous cell carcinomas of the respiratory tract. The dose predicted by the extrapolations from mouse data is higher than the actual dose required in hamster or rat. When squamous cell carcinoma of the respiratory tract is the chosen endpoint, mice are less sensitive to 3-MC than rats or hamsters (see Fig. 3.2.1). However, mice develop adenomas at lower doses than they would develop squamous carcinomas. In c) Mice and rats developed skin tumors. No effect was observed in hamsters, therefore, one percent incidence was used to extrapolate the dose from mice to hamster. The extrapolated doses are lower than the observed dose. Again as in Fig. 3.3.1a, this extrapolation over-estimates the potency of 3-MC. In d) Extrapolation from mouse to monkey or extrapolation from hamster to monkey over-estimates the potency of 3-MC in monkey.

more readily than squamous cell carcinomas. When no distinction is drawn between adenomas and squamous carcinomas, there are no striking differences in sensitivity of the two species based on constant weight or constant surface area extrapolation.

Despite the technical difficulties described above, we have interpreted the large differences between the potencies as genuine differences between species.

We have used *Incidence/mg* as a standard form to compare potency under different experimental conditions. The implicit assumption behind this data transformation is that the incidence of tumors is linearly dependent on the total dose of the toxicant administered to a given animal. Unfortunately, we cannot test the accuracy of this assumption, thus, the transformation may introduce some error.

All of the comparisons reported here were based on experiments administering 3-MC. We have chosen this compound because the best dataset was available for this compound. We have arrived at similar conclusions after we analyzed experiments using B[a]P, although, this data set was less complete. (Results on B[a]P are not reported here). We have assumed that what holds for 3-MC and B[a]P also holds for other PAH.

4.2 Discussion of the results

The potency of a PAH is affected to a considerable degree by the route by which the PAH is taken up. Most rodents are particularly sensitive to PAH administered via the respiratory system. Mice are also vulnerable to the topical application of PAH. The oral route appears much less sensitive than the respiratory route, but the effects from oral administration are detected in tissues at some distance from the site of administration. In contrast, PAH administered topically or to the respiratory system induce effects primarily on that system. The route of administration also affects sites and types of tumor induced by PAH. Since, the potency of PAH and their site of action is significantly affected by the route of administration, the route of exposure should be taken into account during risk assessment.

Table 3.2.1 has several implications for risk assessment. It permits estimation of potency of PAH from a rodent species treated via a particular route to another rodent species with another exposure route. It also shows that the oral as well respiratory tract potencies of 3-MC are reasonably similar across the rodent species. The respiratory system is about 250 times more sensitive than the GI system. This may explain the apparent greater sensitivity in humans to exposure from inhalation than from much higher dietary exposure. It may be prudent to give respiratory exposure 250 times greater weight than the oral exposure, when human risk is being determined.

Potencies of PAH based on rodent to rodent extrapolation (based on body weight or surface area) were significantly different from the experimentally determined potencies. Extrapolations from rodents to monkeys produced errors of many orders of magnitude. It is likely, that the estimates of PAH potency in humans based on surface area or body weight extrapolations from rodent data could lead to very substantial errors. Therefore it is preferable to use other approaches in order to estimate human risk.

Unlike route to route comparisons, we have made our comparisons between species using the homologous site and/or type of tumor whenever possible. As a result, the observed differences between species apply only to the particular endpoint monitored. Thus, even though mice may be more sensitive to forestomach squamous tumors than other rodents, it does not imply that mice would be more sensitive to mammary tumor induction than, say rats.

Because of the importance of these extrapolations for risk assessment, experiments designed to confirm our conclusions are highly desirable.

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Environmental Health Risks of Lead in Ontario: A Multimedia Exposure Assessment[1]

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I Introduction

Although significant gains have been made towards the reduction of lead exposures to the general population, lead nevertheless remains associated with a level of public health concern (Mushak et al., 1990; Silbergeld, 1989; Lee and Moore, 1990). This is due to its widespread presence in the environment and an evolving understanding of its toxic impact at even very low doses, particularly for the fetus and young children (Needleman, 1990; Davis and Sversgaard, 1987).

Because of the presence and persistence of lead in diverse environmental media, adequate risk assessment, therefore, requires consideration of specific lead exposures and their relative contributions to the total lead exposure picture of higher risk population groups.

The present paper describes ongoing work within the Hazardous Contaminants Branch to assess potential exposures to lead and associated risk in Ontario populations utilizing a multimedia approach. Utilizing both deterministic intake and integrated biokinetic\uptake modelling, exposure estimates for sensitive subpopulations are developed based upon environmental levels and trends of lead within various exposure pathways. Preliminary estimates of lead intakes are described. The exposure modelling is evaluated against what is known regarding measured blood lead distributions in Ontario children. Lastly, with reference to current findings regarding the effects of low level lead on the developing central nervous system, a number of conceptual paradigms for interfacing of exposure findings to regulatory strategies (e.g. standards developments) are briefly outlined. This paper is limited to general exposures for young children and pooled adult groups. Other subgroups (women of child bearing age, infants 0-6 months, etc), and scenarios based on location or special exposure sources (e.g point source impact assessment, lead-based paint exposures) are important exposure questions which we have modelled but are not presented here to allow for a more detailed discussion of the general modelling approaches and assumptions.

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[1] The views and ideas expressed in this paper are those of the author and do not necessarily reflect the views or policies of Environment Ontario

II Exposure Assessment

Various approaches can be applied to the problem of assessing the exposure to lead of human populations. Broadly speaking this is achieved either through 1.) environmental monitoring and subsequent modelling of pathway-specific intakes and 2.) population-based studies involving biological monitoring. In the first approach levels and trends of lead is measured/modelled in an environmental media and combined with models of consumption and contact to generate age-specific estimates of intake. In the latter approach lead is measured directly in the receptor in a biological media, typically blood lead (Pb-B) or lead in bone.

Modelling of lead exposure using environmental levels data has evolved such that more than one form is available. A commonly utilized and simplistic approach involves point or deterministic estimates of intake providing values of receptor contact in µg/day or µg/kg/day units. This is referred to here as a multimedia deterministic model. Alternately more complex integrated pharmacokinetic-based models of exposure may be employed

i) Multimedia Deterministic Model

Constructing exposure estimates from the various routes involves consideration of relevant data on the ambient concentrations of lead in each media, data on consumption of and exposure to these media, data on trends in exposure levels over time, and data on uptake and absorption following exposure. Because such data is seldom comprehensive, it is generally the case that assumptions must be made in the estimates of environmental concentrations, rates of intake and absorption factors. As such, the exposure assessment presented is a model which predicts hypothetical doses which are not necessarily encountered. Rough estimates of exposure to "typical" individuals living in Ontario are generated, recognizing that the exposure of any specific individual may vary widely from these estimates according to factors such as age, activity, and geographical location.

Integrated estimates of total daily intakes for children (1-4 years) and adults- derived from summation of individual pathway point estimates- are presented in Table 1. Estimates for 1985 versus current estimates are provided to illustrate the dynamics of change which must be considered in multimedia assessment. The difference derive from changes in the general environmental levels of lead in these media over this period. Young children and adults are predicted to have similar total intakes of lead but different ratios of pathway contribution and children having a much large dose on a µg/kg/day basis (roughly 5 times the adult dosage). Both child and adult doses are predicted to have declined by 25-30% over the past 5-10 years.

TABLE 1: Integrated Lead Exposure Estimates for Urban Ontario Populations

	1985		Present	
	Child (1-4)	Adult (20+ yrs)	Child (1-4)	Adult (20+ yrs)
Food	37.4	53.8	18.1	36.4
Drinking Water	3.0	7.5	3.0	7.5
Air	0.3	1.3	0.15	0.9
Soil/Dust	32.0	8.0	32.0	8.0
Estimated Total (µg/day) (µg/kg/day)	 72.7 5.0	 70.6 1.0	 53.2 3.6	 52.8 0.64

The relative contributions of food, drinking water, air and soil/dust exposures to total intake are indicated in Table 2. For young children, food and soil/dust exposure accounts for the larger part of total intake, with each in the mid-1980's estimated to account for approximately one-half of the exposure each. approximately 4-6% of exposure is through drinking water. A different picture emerges for adults with as much as 80% of exposure through diet and a substantially smaller fraction through dust intake. What is interesting to note here with respect to trends is that while overall intakes has declined equally, the relative contribution pattern has remained relatively static for adults but changed for children. Presently soil/dusts would be suggested to be the greatest contributor to "typical" general exposures for children, with dietary exposure suggested at approximately half the soil/dust contribution.

TABLE 2: Relative Contribution of Media to Total Exposure (%)

	1985		Present	
	Child (1-4)	Adult (20 yrs+)	Child (1-4)	Adult (20 yrs+)
Food	51	76	34	80
Drinking Water	4	11	6	14
Air	<0.1	2	20.1	1
Soil/Dust	45	11	60	15
Total	100	100	100	100

i.a) Dietary Lead

It is generally considered that the primary source of an individual's lead exposure, under most circumstances, is via consumption of food and beverages containing lead. The relative contribution to the integrated lead uptake will be particularly significant for those populations without substantial exposure to other lead sources.

Previous estimates of exposure have suggested a relative contribution of up to 75% of intake for adults and 50% for children (HWC, 1989; MOE, 1991). It is therefore essential to understand the extent, nature and trends in this particular intake. It is relatively clear that lead in food exposure has changed in Canadian and U.S. populations during the 1980's. Estimated food intakes for various time periods are provided in Table 3 for Ontario/Canadian individuals versus U.S. diet figures.

TABLE 3 Lead in Food Exposure Estimates

	Canada/Ontario		U.S. Food and Drug Administration	
Year	Intake µg/day (µg/kg/day)			
	Child (1-4)	Adult (20+)	Child (1-4)	Adult (20+)
1980			38.5	
1982	37.4(2-6)[1,2]	63.8 (0.9)[1] 53.8 (0.8)[3]	2 5	
1984			19.9	82[5]
1986	18.1(1.2)[2]	36.4[4]	12.5	
1988			4.75	

Based on average Ontario Food Consumption Figures from Nutrition Canada Survey

1. Foods Directorate, Health and Welfare Canada
2. MOE, 1991. Based on total diet survey data.
3. Dabeka and MacKenzie, 1987. Duplicate diet.
4. Dabeka, 1991. Total Diet Survey.
5. Gartrell et al, 1985.

It would appear on the basis of U.S. FDA data that a trend towards lower levels of lead in food, and therefore dietary intake of lead, is occurring. This is most notable for young children. Similar trends are suggested by Canadian data, although systematic determination of declines in levels of specific foodstuffs has not been assessed. Such trends have been attributed to primarily three factors: 1.) reductions in ambient particulate fallout to crops as a result of phased-out leaded gasoline; 2.) manufacturers phasing out of use of lead solder in food tins; and 3.) decline in concentrations in waters used in processing and preparation. Comparison of U.S. and Ontario estimates for children gives rise to interesting interpretational questions. Canadian estimates are generally significantly higher than U.S. figures. What may account for this difference and to what degree would a large difference be expected? This may in part be due to 1.) earlier phaseout of leaded gasoline in the U.S. 2.) greater frequency of U.S. basket surveys 3.) differences in study methods and 4.) differences in consumption patterns for specific food types. On the other hand some similarity in intakes might be expected particularly if comparing, for example, Northeastern states to Ontario. Many foods may be obtained from common sources for both populations, and reliance on locally grown foods is probably less significant than in the past.

i.b) Lead in Drinking Water

In order to develop a point estimate of average daily consumption of lead from drinking water, it is necessary to select from the available, a concentration which best approximates the "average" concentration of lead in Ontario drinking water. A value of 5 µg/L (range 1.1 to 30 µg/L) is selected based on the 4.8 µg/L mean concentrations from the recent Ontario composite sampling survey (MOE, 1988). This data was felt to be most representative because: 1) the seven municipalities were selected to reflect major population areas and communities where representative range lead levels had been found or expected; 2) the results from the composite samples were usually much more consistent than grab samples, especially where elevated levels were found and; 3) the composite sample is linked to the water-use patterns of the residents as it samples a portion of the drinking water which is actually consumed by the household. It is a value which falls between the mean median concentration of flushed (3-4 µg/L) and overnight (6.1 µg/L) samples in the Drinking Water Surveillance Program (DWSP), as well as between the flushed (3.3 µg/L) and random/overnight levels (7,6.6 µg/L) of the Northern Ontario Blood Lead study (Goss Gillroy, 1988). The selected value also takes into account the considerable drop in concentration, which occurs in a standing sample following running of the tap.

Based on average daily consumption rates, the average daily intakes of lead from drinking water are calculated to range from 3.0 µg/day (0.21 µg/kg bw/d) for children to 7.5 µg/day (0.11 µg/kg bw/d) for adults. These figures correspond with those recently determined in a similar analysis by the Federal-Provincial Subcommittee on Drinking Water (FPSDC, 1988). Meranger *et al.* (1984), have estimated a daily intake of lead from drinking water to be 0.59 to 0.85 µg.

i.c) Lead in Air

Lead is present in air as a result of current industrial emissions, automotive exhaust and re-entrainment of lead-contaminated dusts. The primary contribution to the overall lead pollution level in air originates from the use of leaded gasolines, whereas fallout from industrial plants that process lead can produce more severe effects on a local scale. Because of the phase out of lead in gasoline within Canada in 1990, it is anticipated, that concern regarding emissions to ambient air will shift almost exclusively to relatively confined localities surrounding significant point sources. The current analysis concerns itself with general population exposure although site-specific scenarios are under development (MOE, 1991).

Routine monitoring of ambient air levels of lead is carried out by the Ontario Ministry of the Environment (MOE) in locations throughout Ontario. Among the results which bear consideration are 1.) the ten-year trend for annual geometric mean lead particulate levels demonstrates substantial decreases, from 0.4 µg/m^3 in 1978 to 0.1 µg/m^3 in 1987 (MOE, 1988) 2.) annual geometric mean values for 1989-90 are generally below 0.05 µg/m^3 Pb across the province; 3.) for most rural locations, the annual mean is 0.05 µg/m^3 or less.

From this most recent information the lead concentration level selected for the exposure analysis is 0.05 µg/m^3 for urban location (non-point source) to reflect an "upper limit" of annual means for urban localities (most cities are in the 0.1- 0.3 µg/m^3 range. Rural would be expected to have even lower levels, because of much lower traffic densities and lack of proximity to industrial lead emissions.

The inhalation exposure analysis for various subgroups living in urban areas, not in the vicinity of a point source, are presented in Table 4. In order to account for differences in exposure encountered indoors as opposed to outdoor time weighted average concentrations have been estimated using the assumption of time spent indoors indicated in the table. According to the U.S.EPA Air Criteria Document (1986), a range of indoor/outdoor air lead concentrations have been determined for different cities and building types, and these vary between 0.3 and 0.8. The value utilized in this analysis is 0.5 reflecting the approximate midpoint of this range. This ratio will be affected by a number of parameters including lead particle size, housing conditions, seasonal changes in activities about the home and meteorological conditions, particularly winds and rainfall. For point sources, where generally larger less mobile particles are involved this ratio has been estimated at 0.3 (Cohen and Cohen, 1987).

TABLE 4: Estimated Daily Intakes of Lead via Inhalation for Ontario Urban Populations

	POPULATION SUBGROUP			
	INFANTS (0-1 yr)	CHILDREN (1-4 yr)	CHILDREN (5-11 yr)	ADULTS (20 yr & +)
Air lead concentration ($\mu g/m^3$)	0.05	0..05	0.05	0.05
Indoor/outdoor concentration ratio	0.5	0.5	0.5	0.5
Time spent outdoors (hours)	1.5	3.0	5.0	5.0
Time weighted average concentration ($\mu g/m^3$)	0.05	0.06	0.06	0.06
Volume inhaled (m^3/day)	2.5	5.0	9.0	22.0
Inhaled daily intake (μg/day)	0.07	0.15	0.27	0.9

i.d) Lead in Soils and Dusts

Adults and children are exposed daily to dusts as a normal factor in homes, streets, playgrounds and other surfaces to which there is routine contact. As discussed above, U.S. epidemiological studies have demonstrated significant correlations between lead concentrations in soils and dusts and blood lead levels in children (Charney *et al.*, 1983; Bornschein *et al.*, 1986; Rubinowitz *et al.*, 1985). It has been suggested that the most probable environmental exposure pathway for young children in soil lead > house dust > hand dust > ingestion > blood lead. The direct ingestion of soil lead in the outdoor environmental will also occur for some children.

Analysis of the exposure to soil and dusts require some knowledge of the concentrations of lead in these media and recognition of the inter-relationship of air, soil and dust lead. Many factors will influence the intermedial distribution of lead including particle size, climatic conditions, surface water solubility of the soil matrix and time (U.S.EPA, 1988). Although lead in soil is relatively immobile it serves as a continuous source of lead in outdoor and indoor (household) dusts, as the upper layer of soil is subject to re-entrainment bv wind and human disturbance.
This very top layer of soil to which people can be directly exposed, is sometimes referred to as "soil dust" (U.S.EPA 1985,

1988). The other components which contribute to the quantity of lead in dusts are direct deposition from the atmosphere - the primary sources being motor vehicle and industrial emissions - and the weathering or renovation of lead-containing paint work. Few data are available, however, from which to make inference regarding the relative contribution by source to dusts.

The interplay of soil, dust and air lead concentrations has recently been analyzed in the US EPA integrated uptake biokinetic model of lead exposure (EPA, 1988). Available studies that included both measurements of air lead levels and soil/dust concentrations were utilized to develop a prediction of the rate of change in soil and indoor dust lead as a function of ambient air lead levels. The key underlying assumption is that changes in air lead will be followed by corresponding changes in soil lead and house dust concentrations. The following long-term equilibrium relationships where suggested:

$$\text{Soil Lead} = 50.1 + 579.0\ (\text{Ambient Air Lead})$$
$$\text{Dust Lead} = 57.6 + 972.0\ (\text{Ambient Air Lead})$$

In the short term (several months or less), changes in ambient lead were predicted to result in direct changes only in dust lead levels, but little or no change in soil lead levels.

These equations would predict a ratio for soil to dust lead concentrations of 1:1.7, at a given air concentration.

A summary of MOE data collected between 1972 - 1982 in areas not impacted upon by industrial point sources indicated mean values of urban, small town and rural areas of 123 µg/g (5-845 range), 73 µg/g (2-133 range) and 35 µg/g (<5-360 range) respectively (Rinne, 1989). Examples of specific urban (pop. > 10,000) residential mean concentrations, derived from pooled 1972-1985 MOE data are 121 (+142) µg/g for Toronto, 119 (+95) µg/g for Windsor and 150 (+93) µg/g for Guelph. For the City of Toronto, the range of values among 233 samples was 5-845 µg/g lead in soil. The sampling from which the above figures and the "upper limit of normal" for soil lead in urban areas are derived consist largely of composite sampling (10-12 samples per residence) taken at 0-5 cm depth. The cities indicated were considered to have the most extensive sampling databases.

Typical house dust levels in Canada of 50-400 µg/g in suburban locations have been reported (Nriagu, 1986). In 1973, house dust concentrations in a Toronto urban control area were measured at a mean of 845 µg/g with a range of 351-2010 µg/g (Roberts et al., 1975). There are no more recent data on lead concentrations in household dust in Ontario and Canada. Information on house dust lead concentrations is quite sparse, particularly information on spatial and temporal variations in levels in houses (Duggan and Inskeip, 1985). This, coupled with a lack of any standardized methodology for representative house dust sampling and analysis, make interpretation of dusts data highly problematic.

Insufficient data is available to separate, in a quantitative manner, relative exposures to lead in soil versus lead in dusts and therefore these must be considered together. Because of evidence pointing to the importance of dusts as a critical path of exposure, because generally a larger proportion of time is spent indoors by children, and because house dust lead concentrations may exceed soil lead concentrations, house dusts are taken as the surrogate exposure vehicle for all soil and dusts. Because of the lack of data on house dust levels, the concentration used are derived by application of the soil dust lead ratio (arbitrarily rounded to 2 from 1.7) to soil lead concentrations selected to be representative of urban (200 µg/g) locations in Ontario. The calculated urban value of 400 µg/g lead in house dust is the upper value of the range of Canadian suburban household dust lead levels reported by Nriagu (1986). A recent analysis by Health and Welfare Canada estimated household dust lead concentration in Canadian urban communities at 350 µg/g based upon the observed declines in the average concentration of lead in soil (43%) and air (73%) between 1973 and 1985 (HWC, 1989).

For the present exposure assessment a soil/dust ingestion figure of 80 mg/day is assumed for children 1-4 years old. No information empirical was found which would provide a basis for estimating amounts of soil eaten by older children and adults. Exposure scenarios which include soil ingestion for adults assume that adults ingest less soil than children, because of differences in behaviour and personal hygiene. Adults are assumed here to ingest 20 mg of soil daily.

ii) Integrated Uptake/Biokinetic Model

An alternate method to deterministic approaches is presented by models incorporating considerations of absorption (uptake) dynamics and distribution kinetics of lead into various tissue compartments. The Integrated Uptake/Biokinetic Model (IU/BK) developed by Harley and Kneip has been utilized by U.S.EPA in development of lead standards/guidelines (U.S.EPA, 1990). The IU/BK Model accepts monitoring data or modeled levels of lead in media associated with various exposure pathways (soil/dust, diet, water, air) and utilising age-specific intake and uptake parameters predicts total lead uptakes. These lead uptakes are then transformed to mean blood lead levels, which together with a geometric standard deviation can be used to estimate the frequency distribution of blood lead levels in children (U.S.EPA, 1989). This is a most valuable parameter for the purposes of lead risk characterization. Site-specific source contributions to blood lead levels and contributions from all media may also be examined. Although originally designed with focus on site-specific situations (e.g. vicinity of lead processing plant), broader application may be feasible.

Using the same environmental levels and media-specific consumption parameters from the deterministic multimedia model, predicted blood lead distribution in children were generated through the IU/BK model. Default biokinetic slope factors and transfer coefficients were utilized. Calculated blood lead and media uptakes were generated yield values and plots shown in Table 5 and Figure 1 respectively. In general dietary and soil/dust uptake contribute the greater portion of the integrated exposure. The question of how exposure and therefore populations blood lead may be changing over time given recent centralized control mechanisms, was examined for three time periods (early-mid 1980's, late 1980's and 1990's). For a choice of a blood lead cut-off value of 10 µg/dL, the modelling suggests a dynamically changing exposure picture from large percentages above this cutoff in the early 1980's to relatively small, to perhaps less than 1% for the 1990. This of course does not account for incidental exposures, (for example to lead-based paint) or point source impacted areas where individual blood leads may be notably elevated. These changes are driven by estimated reductions in dietary and airborne lead concentrations.

It is interesting to roughly compare the predictions of the model with epidemiological data of blood leads for Ontario child populations. The model predicts a geometric mean blood lead of 8.7 µg/dL as opposed to 12.02 observed in urban children of the 1984 Ontario Blood Lead Study (Duncan *et al.*, 1985). A higher degree of prediction is seen with later 1980's data, where the IU/BK model estimates approximately 6 µg/dL as opposed to a mean 7.87 observed in urban Northern Ontario children in 1987 (Goss, Gilroy, 1988). The differences may be possible due to: 1.) underestimation of exposures related to diet for dusts 2.) underestimation of absorption of ingested inorganic lead or 3.) inability to adequately account for incidental exposures related to lead-based paints or other common product sources. The degree to which this model is applicable to broader population analysis as opposed to site-specific questions requires further consideration. However, it is apparent that this tool can provide a useful aid to integrated analysis and risk-based decision-making for lead.

Table 5 IU/BK Model: Calculated Blood Lead and Relative Media Uptakes for Children (Non-Point Source)[1]

Time Period	Age	G.M. Blood Level (µg/dL)	Diet Uptake (µg/day)	Water Uptake (µg/day)	Soil/Dust Uptake (µg/day)	Air (µg/day)	Total (µg/day)
early-mid 1980's	1-2	8.1	18.7	1.4	9.1	0.16	29.4
	2-3	8.4	18.7	1.4	9.1	0.27	29.5
	3-4	8.5	18.7	1.4	9.1	0.28	29.5
late 1980's	1-2	6.3	9.1	1.4	9.1	0.05	19.6
	2-3	5.7	9.1	1.4	9.1	0.09	19.7
	3-4	5.7	9.1	1.4	9.1	0.09	19.7
199??	1-2	4.8	5.0	1.4	6.9	0.03	13.4
	2-3	4.6	5.0	1.4	6.9	0.05	13.4
	3-4	3.9	5.0	1.4	6.9	0.05	13.5

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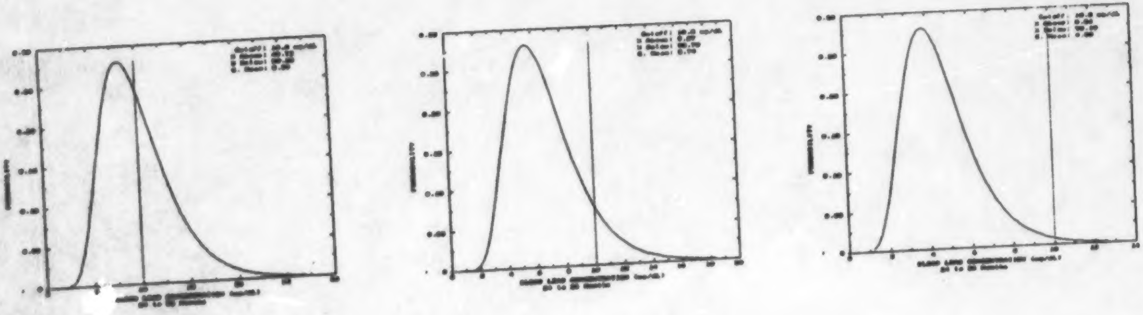
[1] Linear absorption methodologies utilised

FIGURE 1: IU/BK Predicted Trends in Blood Lead Frequency Distribution
early 1980's-1990's



Early-mid 1980's

Late 1980's

199?

III Toxicological Consideration

Discussion of the myriad of literature associated with the health effects of lead is not attempted here. Very briefly, over the past two decades, understanding of childhood and prenatal lead toxicity has changed substantially and the generally recognized level for lead toxicity has evolved downward. Blood lead levels as low as 10 µg/dL, and perhaps lower, have been associated with decreased intelligence and impaired neurobehavioural development. Effects on stature and hearing acuity have also been suggested at low PbB levels. The Centre for Disease Control is currently considering downward revision of its current community intervention level of 25 µg/dL blood lead. With respect to the subclinical neurotoxicity of lead, a number of investigators are now questioning whether such effects may diminish continuously as exposure decreases to zero that is, that there may not be a threshold for effects. This has brought into question the historical assumption of the general existence of thresholds for non-cancer adverse effects.

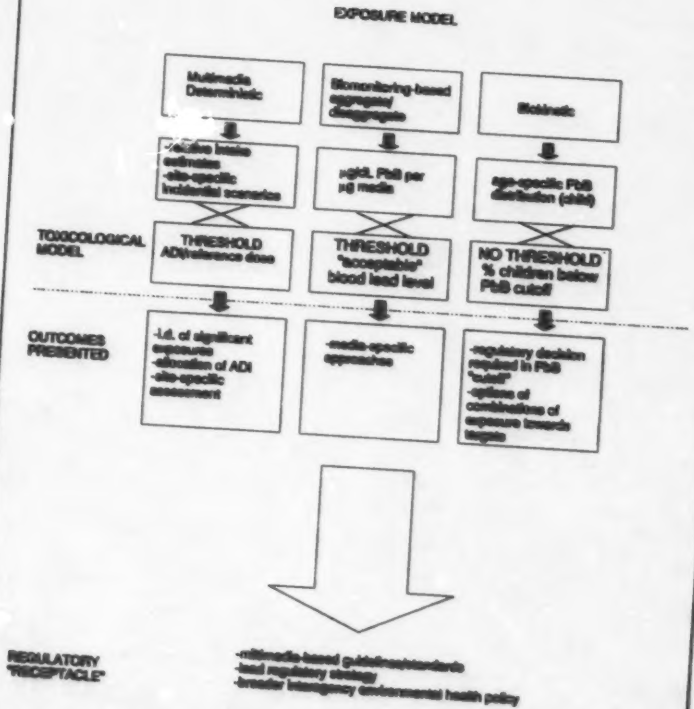
U.S.EPA has recommended against establishment of a reference dose for lead. In contrast other agencies have supported a threshold approved through development of provisional tolerable intake values (e.g. the FAO/WHO permissible tolerable weekly intake is 25 µg/kg or daily intake of 3.5 µg/kg/day, 52.5 µg/day for a 15 kg child). Typically a safety factor of 1.5-2 is applied in this type of derivation.

Comparison of total integrated intakes for Ontario with these threshold values suggests that on average in the early 1980's, typical total exposure for children would have exceeded these levels. Similarly mean values for urban children from Ontario blood lead studies of this period were slightly greater than the 10 µg/dL PbB value currently being associated with potential subclinical effects. Modelling using more recent intake data suggest total intakes approaching or very slightly greater than the WHO PTWI. Predicted PbB from biokinetic modelling suggest lower mean values for late 1980's and the current decade. Although it is likely that overall exposures will continue to decline, particular incidental exposures like lead-based paint and exposures in communities impacted by stationary sources of lead continue to be of concern, in light of the continuing evolution downward of blood lead levels associated with effect.

IV Regulatory Application

Detailed multimedia risk assessment has been undertaken by the MOE Hazardous Contaminants Branch to provide the scientific basis for the development of standards/guidelines for lead in single media (air, soil/dust, drinking water), working from a multimedia analysis framework. Differing approaches/tools towards the exposure assessment and toxicological consideration create a matrix of scientific information for application to standards development as well other broader regulatory strategies for lead. Such a

FIGURE 2: Conceptual Matrix for Multimedia Risk Model – Regulatory Interface


EXPOSURE MODEL
Multimedia Deterministic
Biomonitoring-based aggregate/ disaggregate
Biokinetic
-relative intake estimates
-site-specific incidental scenarios
µg/dL PbB per µg media
age-specific PbB distribution (child)
TOXICOLOGICAL MODEL
THRESHOLD ADI/reference dose
THRESHOLD "acceptable" blood lead level
NO THRESHOLD % children below PbB cutoff
OUTCOMES PRESENTED
-i.d. of significant exposures
-allocation of ADI
-site-specific assessment
-media-specific approaches
-regulatory decision required in PbB "cutoff"
-options of combinations of exposure towards targets
REGULATORY "RECEPTACLE"
-multimedia-based guidelines/standards
-lead regulatory strategy
-broader interagency environmental health policy

matrix is suggested in Figure 2. Depending on the risk model selected differential risk characterization and therefore different strategic frameworks will be defined. For example, utilization of biokinetic modelling represents a deviation from a reference dose approach but may allow a more flexible approach for developing multimedia sets of guidelines. This approach also raises the question of what is the appropriate unit of risk. Multimedia deterministic models of intake leads to the allocation of a suggested acceptable daily intake, is based on more simplistic methods (and arguably more easily communicated) and fewer model assumptions. Analysis of the relative advantages/disadvantages of various risk models is in preparation.

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B14

THE HAMILTON STUDY: LONG-TERM EFFECTS OF SO_2 AND AEROSOLS ON CHILDREN WITH ASTHMA

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BACKGROUND

Asthma morbidity and mortality.

"Rates of hospital admission/separation for asthma and rates of death from asthma have increased dramatically among children and young adults during recent years in Canada."(1). In the United States, asthma is the most common chronic disease of childhood, affecting 15 percent of Americans under the age of 15. "It ranks first among the chronic diseases in causing school absenteeism, and it has been linked to lowered academic performance."(2) Asthma is the commonest cause for admission to hospital in North America and twice as common as the next most common cause (3). Appropriate diagnosis and treatment reduces morbidity in childhood, and it is possible that good control in childhood may reduce severity in adult life (4,5).

It is not clear whether the increase in morbidity and mortality is a result of increasing prevalence or severity, or by past underdiagnosis and undertreatment, or by a combination of factors. However, there is some evidence in the literature that the respiratory environment plays a role in the pathogenesis of asthma.

Definition and methods of diagnosis of asthma

Asthma has been defined as a disease characterized by wide variations over short periods of time in resistance to flow in intrapulmonary airways (6). Although the definition of asthma in an epidemiologic survey has been a matter of debate, it is felt that the underlying abnormality of asthma is one of increased airway responsiveness (4,7,15). In the absence of diagnostic confirmation using the histamine or methacholine test, or methods of observation of diurnal variation of peak flow (both difficult to implement in the epidemiological context), one must rely on responses given to questionnaires by parents or children themselves, and perhaps the results obtained from pulmonary function tests of the children. This has been a common procedure in epidemiological studies, and estimates of prevalence based on random samples of population have been obtained in this way (8,9,10,11,12,13, 14,15).

Prevalence of childhood asthma.

There is currently limited information about the prevalence of asthma in children in Canada. The study by Becklake and her colleagues carried out in suburbs of Montreal, obtained responses to questions about "wheezing" and past "asthma". The prevalence they obtained in 637 children age 9-10 for "wheezing" was 11.6% (males) and 9.5% (females); for "asthma" was 9.3% (males) and 4.9% (females) (16). A brief note in abstract form provides more recent evidence of a change in asthma prevalence in 3 and 7 year old children in Montreal: 3.8% in 1981 and 6.4% in 1983 (17).

Previous work from this laboratory

The Urban Air Environment Group, Department of Medicine, McMaster University, completed two field studies of the effects of the environment on respiratory health in a cohort of Hamilton school children: the first from 1978-82 (22), and the second from 1982-1986 (24).

The sponsoring agencies for these studies were: Health and Welfare Canada, the Ontario Ministry of Health, and the Ontario Ministry of the Environment. Details of the methods of these studies are given in (10,18,19,20).

In the first study, on three occasions (1979, "Period 1"; 1980, "Period 2"; and 1981, "Period 3"), respiratory health and pulmonary function was measured in a cohort of over 3200 school children whose ages varied from 7 to 10 yr in the Fall of 1978. In the second study, respiratory health and pulmonary function data on those still available from this cohort (over 2000) were obtained twice more, (1983-4, "Period 4"; and 1985-6, "Period 5"). During the latter two periods, biochemically validated estimates were also obtained of the smoking habits of the young people, who by this time were adolescents. From 1979 to 1986 air quality was also measured: Total Suspended Particulate (TSP); Particle Size Distribution (PSD), expressed as Aerodynamic Mass Median Diameter (MMD), or concentration of the fine fraction of suspended particles less than 3.3 um MMD (FF); and Sulphur Dioxide concentration (SO_2). The validity and repeatability of all these data were measured and found to be within acceptable limits (10,18,19). During this time (1982-3) a study of the indoor air quality and the indoor/outdoor relationships of air pollutants in 20 homes and 16 schools was also carried out (21). Some early results have been previously reported (22,24,27).

Effects of air quality on pulmonary function in asthmatic children.
This aspect of the study (arising from an analysis funded by OME), specifically focussed on the asthmatic children found in this cohort, and was recently reported (23,28).

For each pollutant, the children were divided into two groups: those with exposure above the median level, and those below. Each group was further divided into children with a physician diagnosis of asthma, and those without. Comparison of the value of the two pulmonary function variables FEV_1/FVC and MET was made between groups. Data analysed were for what we refer to as "Period 2", corresponding essentially to the calendar year 1980, and the mean age of the cohort at this time was 10 yr.

In the **asthmatic group**, statistically significant and clinically important **increases in airflow obstruction**, as demonstrated by two reliable indicators of pulmonary function, were found to be associated with **increased chronic exposure** to SO_2 at the relatively low levels found in Hamilton during this period (median 10.6 ppb, min - max, 8.4 - 17.5 ppb annual arithmetic mean). This was not observed in the rest of the cohort; in fact statistically significant but not clinically important **decreases** in airflow obstruction were observed in the rest of the group, consistent with the earlier observations with respect to SO_2 we reported in November 1986. The former is a particularly surprising finding, because it demonstrates airflow obstruction in asthmatic children associated with SO_2 exposure levels one to two orders of magnitude less than previously observed for acute exposures in adults.

OBJECTIVE:

To evaluate the hypothesis that chronic low-level exposure to air pollution is associated with the severity of asthma in children. This was carried out in three steps:

1. Using data combined from the two previous studies, three groups were identified from the cohort: "asthmatic"; "wheezy"; and "neither asthmatic nor wheezy" children, as

determined from responses to the health questionnaire.

2. Cross-sectional analysis was carried out to determine whether pulmonary function in each of these groups is affected by air quality in a given year, and whether the effects are different for each group.

3. Longitudinal analysis was used to describe the changes in pulmonary function over time in each group, and to determine whether these changes are associated with differences in exposure to air pollution over the same time.

METHODS

The methods used for obtaining environmental and epidemiological field data as well as the data analysis techniques, have been described in the Final Reports of the three previous projects, as well as in previous publications (10,18,19,20). Methods which differ from those previously used will be described here.

Creation of New Variables

Environmental.

For each Period, exposure values (yearly average) for TSP, FF, CF, and SO_2 had been computed separately for each child, and exist as data variables on the data files. For the longitudinal analyses it was necessary to calculate exposure values for the whole period of study, i.e. Periods 1 to 5. Thus the Period 2 exposure would relate to growth between Periods 1 and 2, Period 3 to growth between 2 and 3, etc. Thus a single value for exposure to be used in the Period 1-5 analysis was obtained by taking the sum of the exposures in Periods 2,3,4 and 5 (e.g. $TSP_{1-5} = TSP_2 + TSP_3 + TSP_4 + TSP_5$).

Epidemiological.

For each pulmonary function variable of interest, for each analysis group and sex, data were extracted from the combined file to give a value for each child obtained in each Period of data gathering. Thus for most children there were, for example, five observations of height, FVC, etc. which were separated in time by intervals of varying length, and so the date of the test for each measurement was also extracted, to obtain the time elapsed between tests. A linear regression model of pulmonary function on time was fitted to the five data points, and the slope coefficient was tested to determine whether it was different from zero ($p < 0.05$). A set of data were created for each child which included a code for significance, and the values of the slope and intercept of the regression. These data, for all pulmonary function variables of interest were output in a file which was then recombined with the original data file, and subsequently used as new dependent variables. This represents the first stage in the type of analysis described as the "Standard Two-Stage" or "STS" by Feldman (25).

Creation of groups

For each child, 3 additional new variables were created: "NORMAL", "WHEEZE", and "ASTHMA". If a child had been coded as having had asthma (Q4 in Periods 1,2,& 3, ASMANOW in Periods 4 & 5) during any of the Periods, the ASTHMA variable was set to a value of '1', otherwise it was '0'. If a child had been coded as having had a wheeze (Q3 or WHEEZY) during any of the Periods, and had not been coded as having asthma during any of the Periods, the WHEEZE variable was set to '1', otherwise it was '0'. And finally, for those children who had not been coded as having either asthma or wheeze during any of the Periods, the NORMAL variable was set to '1', otherwise it was set to '0'. The new variables were included in all 6 main files: the 5 cross-sectional files (Per 1, Per 2, Per 3, Per 4, and Per 5), and the longitudinal file (Per 1-5).

The assumption underlying the design of this study was that asthmatic or "wheezy" children were more likely to experience a decrement in pulmonary function as a result of a chronic exposure to air pollution, than would children not expressing these symptoms, i.e., "normal" children. It was also assumed that those characteristics which would make these children more sensitive would be present during the whole period of seven years that we followed them. Thus at any given Period, a child in the ASTHMA group, for example, may not necessarily express that symptom or descriptor during that period, but we assumed that they were still more sensitive than a normal child to the effects of air pollution. This assumption was based on results of the cross-sectional study (28). If this assumption held true, then for a given cross-sectional analysis in any Period, the sample size for the ASTHMA group would be larger than that for the children who expressed asthma only for the year previous to testing in that Period.

In Period 2 we had the largest number (347) of children who, to our knowledge ever had asthma over the 7-year period we followed them. In that Period, however, only 131 children were said to have had asthma in the year prior to our testing them.

Three sets of new sub-files were created from each cross-sectional file (except Per 1) which contained only children (both sexes) from each group, i.e. ASTHMA, WHEEZE, or NORMAL, and which included selected pulmonary function and questionnaire variables, together with the relevant exposure variables. Thus 12 sub-files for the cross-sectional analysis were created. For the longitudinal file (Per 1-5), because of the size of the file, the 3 groups were separated into males and females, giving 6 sub-files. The variables selected for analysis from the Per 1-5 file were the slopes, intercepts and significance variables, some selected questionnaire variables, and the longitudinal exposure variables.

Statistical Analyses
Statistical analyses were performed using the statistical package SAS-PC (26), implemented on a Hewlett-Packard computer (Vectra RS 20C). These included descriptive statistics, comparison of sample means and comparison of observed with expected frequencies, as well as stepwise multiple regression analysis. Comparison of sample means was carried out using the procedure of analysis of variance. For this purpose new binary independent variables were created to represent the air pollution variables. This was done by determining for the cohort as a whole the median value for exposure of a given pollutant, and for each child setting the value of the new variable at "1" if the exposure for that child was equal to or greater than the median value, and "0" if the exposure for that child was less than the median for the Period under study. For each pollutant, and for each Period, the median of all of the 12-month mean values of calculated exposures is given in Table A.

Table A. MEDIAN EXPOSURE

Period	CF ug/m3	FF ug/m3	TSP ug/m3	SO_2 ppb
2	42.5	45.4	51.5	10.6
3	39.4	45.9	46.4	9.2
4	46.8	52.2	47.1	11.6
5	39.0	44.6	45.7	6.8

Cross-sectional Analysis
The mean value of the pulmonary function variable of that part of a group of children (e.g. ASTHMA) whose exposure was equal to or above the median was compared to that of the part whose exposure was below the median. Using this technique the influence of each pollutant on pulmonary function was determined separately. This provided a simple test of limited sensitivity as a preliminary stage in the analysis.

In the second stage of the analysis the effect of one or several independent variables on a continuously distributed dependent variable was performed by multiple regression using SAS. The conventional level for statistical significance (that is, the probability that the association may have occured by chance, or 'alpha') taken in this report is 0.05.

Longitudinal Analysis
For each pulmonary function variable of interest, stepwise multiple linear regression analysis was carried out in the "wheeze" and "normal" groups only, using slope or intercept of the regressions of the 5 Period values of that variable as a function of time (as described above) as the dependent variable in those children in whom the longitudinal regression was found to be significant, the others being declared "missing" for the purposes of this analysis. The independent variables used in this analysis were: Period 2-5 TSP, FF, CF, SO_2 (as continuous variables), and Period 2 maternal smoking and gas stove use, as well as self-smoking in Periods 4 or 5 (all the latter as binary variables).

RESULTS AND DISCUSSION

Selection of Groups

We have from our cohort of 3579 schoolchildren, 3 groups, identified as ASTHMA, WHEEZE and NORMAL on the basis of response to a symptom questionnaire. The children were studied on 5 occasions over a period of 7 years, during which their exposure to air pollution was also measured. From these, 1426 children had valid measurements at all 5 occasions.

Analysis of pulmonary function data cross-sectionally showed that both the ASTHMA and the WHEEZE groups showed statistically significantly increased airflow obstruction when compared to the NORMAL group. Analysis of the data longitudinally showed that the ASTHMA group differed significantly from the NORMAL group in the rate of growth of pulmonary function.

Cross-sectional analysis

Neither the ASTHMA group nor the WHEEZE group showed the strong and systematic associations of air pollution with reduction in pulmonary function that were expected from year to year; there were, however some reductions in pulmonary function found to be associated with elevated exposure to SO_2 and CF.

The NORMAL group showed the most consistent negative responses both to the exposure to the effects of maternal smoking, and to the exposure to FF and SO_2. These findings, taken together, suggest that for a cross-sectional analysis, if there is an increased sensitivity of children with asthma or wheezy breathing to the effects of air pollution, the inherent variability of airway function in these children, compared to children without these symptoms, tends to make its effects difficult to demonstrate. In addition, we have confirmed earlier observations of the association of diminished pulmonary function with increased exposure to aerosol particles in children, and have added to these new evidence of the association of diminished pulmonary function to increased exposure to SO_2 in female but not male children.

Longitudinal analysis

A major objective of this study was to take advantage of the fact that measurements were available on 5 occasions over a period of 7 years in over 1400 children, with accompanying air quality data. An opportunity existed to examine the growth of pulmonary function in these children, and to determine whether air pollution had an influence on growth, and whether children with asthma were at a greater risk than children without asthma of any negative effects of air pollution on growth of pulmonary function.

Stepwise multiple linear regression analysis of the WHEEZE and NORMAL groups yielded mixed results, showing negative associations between rates of growth of pulmonary function and CF, but positive associations with FF and TSP. Further analysis needs to be carried out to gain an understanding of this phenomenon.

Figures 1 and 2 show that there are negative effects of exposure to CF and SO_2 on the growth of pulmonary function in children with asthma. Figure 3 shows that both children without asthma as well as children with asthma suffer a reduction in pulmonary function associated with increased exposure to CF, but that the growth of PF is least in asthmatic children with increased exposure to CF. In all cases in the ASTHMA group where statistically significant associations were observed between rate of growth and air pollution, they were negative; i.e., a reduction in rate of growth associated with an increase in air pollution exposure.

CONCLUSIONS:

1. Three groups of children were identified: ASTHMA, WHEEZE and NORMAL; and it was found that significant differences in pulmonary function measurements were observed between these groups. Children with asthma showed a reduced growth of pulmonary function, over a 7-year period, compared with normal children.

2. Cross-sectional analysis of data in the ASTHMA group showed no greater sensitivity to air pollution than shown in asthmatic children from previous analyses of data from this study. NORMAL children, however showed significant decrement in pulmonary function in association with higher levels of exposure to FF, SO$_2$, and maternal smoking.

3. Longitudinal analysis showed consistent reduction in rates of growth of pulmonary function associated with elevated values of CF and SO$_2$ in the ASTHMA group, as well as a reduction in growth of pulmonary function associated with elevated values of CF in the NORMAL group. The WHEEZE and NORMAL groups also showed some increments in rates of growth associated with FF and TSP that require further analysis to assist in their interpretation.

FIGURE 1

FIGURE 2

CF EXPOSURE AND LUNG GROWTH
IN CHILDREN WITH ASTHMA

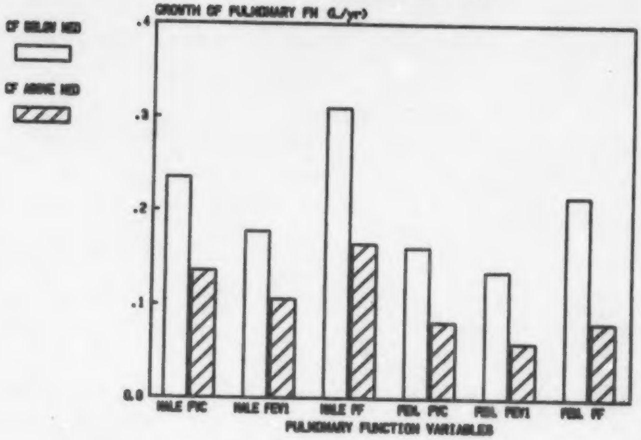
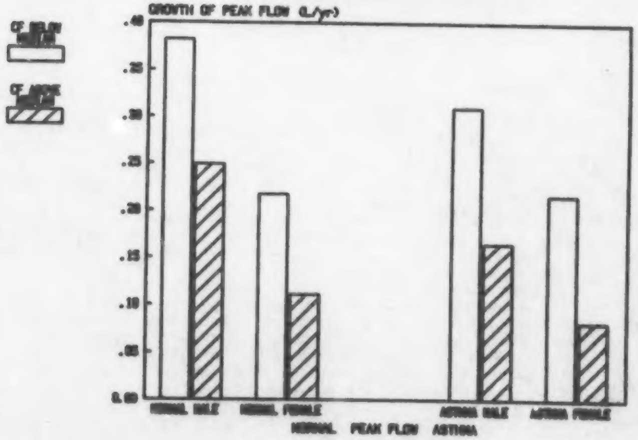


FIGURE 3

CF EXPOSURE AND LUNG GROWTH
IN NORMAL & ASTHMATIC CHILDREN



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B16

SURVEY OF COMMUNITY ACCEPTANCE OF AIR CONDITIONER NOISE

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Introduction

This paper is a brief summary of a survey of the subjective disturbance due to outdoor residential air conditioner noise. The survey included noise measurements of ambient and outdoor air conditioner noises as well as interviews of 550 subjects in the Metropolitan Toronto area. Measurement sites were chosen to include subjects from the four combinations of high and low ambient noise, as well as owners and non-owners of air conditioners. All sites consisted of detached single family homes with some of the homes having outdoor central air conditioning or heat pump units.

Noise measurements included 30 second integrated A-weighted sound levels measured at the following locations: at 6 feet from the air conditioner source, at the neighbour's property line, at the facade of the neighbour's house, and at the neighbour's outdoor patio area. Day, night and 24 hour A-weighted L_{eq} measurements were made of existing ambient noise levels near to the road in front of the subjects homes. Subjective responses were obtained by interviewer-administered questionnaires in the homes of subjects living next to owners of air conditioners. The questionnaire included a few initial open questions but consisted mainly of questions to directly elicit the frequency of hearing various noises and the subject's annoyance to these noises. Questions were asked concerning road traffic noise, train noise, aircraft noise, and air conditioner noise for conditions when the subjects were both inside and outside their home in the day-time or the night-time. Thus, there were eight different questions about each of the four types of noises.

Table 1 summarizes the means and standard deviations of the measured noise data. Table 2 includes information concerning the subjects in the survey. Forty-four percent of the subjects were male and 56% were female.

Air Conditioner Noise	Mean	Std Dev
Source level, dB(A)	64.3	3.0
Property line level, dB(A)	60.1	4.8
Facade level, dB(A)	58.3	4.7
Patio level, dB(A)	55.8	3.9
Background level, dB(A)	53.5	3.9
Ambient Noise levels		
Day-time L_{eq}, dB(A)	61.2	3.3
Night-time L_{eq}, dB(A)	54.5	3.5
24 hour L_{eq}, dB(A)	59.7	3.2

Table 1. Summary of measured noise level values.

Variable	Mean	Std Dev
No. adults	2.33	.91
No. young people	1.07	1.37
Age	40.74	13.02
Family income	$45,900	$24,400
Years of education	14.31	3.59

Table 2. Summary of socio-economic survey variables.

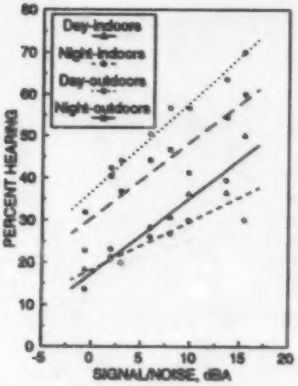

Figure 1. Percentage of subjects hearing air conditioner noise versus property line signal/noise ratio.

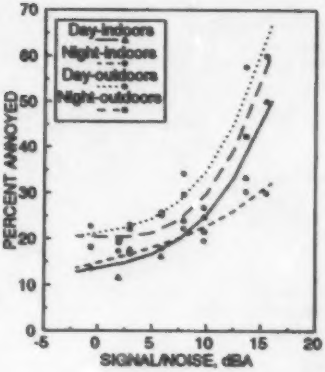

Figure 2. Percentage of subjects annoyed by air conditioner noise versus property line signal/noise ratio.

Grouped Responses

Subjective responses were generally most strongly related to air conditioner noise levels at the property line. Grouped data were created by dividing the subjects into eight groups according to A-weighted noise levels at the property line with each group having a 3 dB(A) range. The percentage of subjects reporting hearing or being annoyed by various noises was then calculated. These group scores concerning the frequency of hearing and annoyance to the noise of the neighbour's air conditioner were strongly correlated with noise levels at the property line. The frequency of hearing the neighbour's air conditioner related linearly to the measured air conditioner noise levels at the property line; the frequency of annoyance related best to the cube of the noise levels at property line.

Responses were more strongly related to the amount by which the air conditioner noise exceeded the background noise with the air conditioner turned off. This level difference is referred to as the air conditioner signal/noise ratio. Figure 1 plots the frequency of hearing the noise of the neighbour's air conditioner versus this signal/noise ratio for air conditioner noise measurements at the property line. Responses are approximately linearly related to the signal/noise ratios; air conditioners were heard more frequently when outdoors, and tended to be heard more frequently during the day-time. Figure 2 shows the frequency of annoyance to be more closely related to the cube of the signal/noise ratio measured at the property line. Again, there is a tendency for outdoor responses to be higher than indoor responses and for day-time responses to be higher than night-time responses.

Individual Responses

When individual subject responses were considered, again significant relationships with measured air conditioner noise levels were obtained, but the magnitude of the correlation coefficients was quite small. Both the use of composite response scales and the exclusions of low signal/noise data were used to try to improve the magnitude of these correlations, with little success. The correlations were low because in many cases the air conditioner noise was not much greater than the existing ambient noise. This led to two problems: (1) in some cases, subjects would not be able to hear their neighbour's air conditioner and so could not accurately comment on it; and (2) it was often difficult to measure the air conditioner noise accurately.

Responses were again found to be more strongly correlated with signal/noise ratios than the actual measured air conditioner noise levels, and correlations were strongest with the cube of the signal/noise ratios. Figure 3 shows the best fit regression lines versus the cube of the property line signal/noise ratios for outdoor day-time responses. These and other similar plots show little effect of increasing air conditioner noise below signal/noise ratios of approximately +5 dB(A).

Site Variable Effects

Analysis of variance tests produced significant main effects of both site ambient noise levels (as measured by 24 hour L_{eq} values) and ownership of an air conditioner. Although owners and non-owners had similar air conditioner noise exposures, non-owners were more disturbed. The difference in the mean responses for owners and non-owners was equivalent to an approximate 7 dB(A) difference in property line air conditioner noise levels.

When subjects were divided into low (mean 24 hour L_{eq} 57.4 dB(A)) and high (mean 24 hour L_{eq} 62.6 dB(A)) ambient noise sites, subjects at higher ambient noise sites were less disturbed by the noise of their neighbour's air conditioner. Figure 4 plots the best-fit linear regression lines for reported hearing of the neighbour's air conditioner while outdoors during the day-time versus

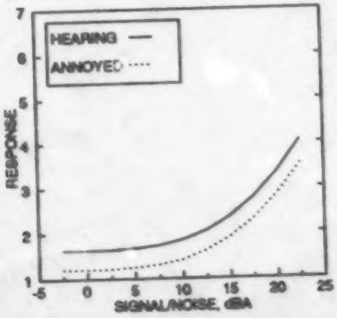

Figure 3. Best-fit regression lines for indoor day-time responses versus property line signal/noise ratios.

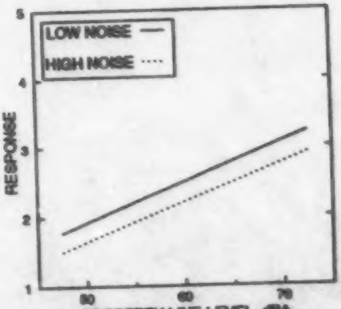

Figure 4. Best-fit regression lines for outdoor day-time responses versus property line signal/noise ratio for high and low ambient noise groups.

the air conditioner noise level at the property line for high and low ambient noise sites. The two regression lines are approximately parallel and separated by about 5 dB(A). This corresponds to the difference in mean 24 hour L_{eq} values for the two groups. Thus, the effect of ambient noise on responses is again explained by a signal/noise effect. For similar air conditioner noise levels, at higher ambient noise sites there will be lower signal/noise ratios and hence less disturbance by the air conditioner noise.

Conclusions

Individual and grouped adverse responses to residential air conditioner noise are most strongly related to the amount by which the air conditioner noise exceeds the existing background noise levels (termed the air conditioner signal/noise ratio in this paper). Subjects at higher ambient noise sites are less disturbed due to lower signal/noise ratios. Owners of air conditioners are less disturbed by the noise of their neighbour's air conditioner by an amount equivalent to an approximate 7 dB(A) difference in air conditioner noise levels.

Below air conditioner signal/noise ratios at the property line of about +5 dB(A), there is little evidence of disturbance being related to air conditioner noise levels. Similarly, adverse responses do not increase with air conditioner noise level at the property line below approximately 50 to 55 dB(A).

Acknowledgements

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VOLUME I

SESSION B

ENVIRONMENTAL EFFECTS

POSTER PRESENTATIONS

DEVELOPMENT OF AN AIRBORNE VIDEO IMAGE-BASED MAPLE DECLINE INDEX

D.J. King* and X.P. Yuan**

SUMMARY

Research on quantitative analysis of airborne digital multispectral videography for sugar maple decline assessment commenced in 1987. Preliminary methodology was developed which utilized both spectral and textural image characteristics of individual tree crowns in the determination of decline. A linear decline index combining both of these was tested and results agreed well with MOE field assessments on a plot-by-plot basis. The objectives of the current phase of this research are to: i) determine the best relationships between selected image spectral/textural measures and ground-based decline symptoms for individual trees, ii) determine the relative accuracy and cost-effectiveness of the video method through comparison with MOE results, and iii) refine the data acquisition and analysis techniques. Data acquired in August 1991 are presently being analyzed to achieve these goals.

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INTRODUCTION

Sugar maple (Acer saccharum) decline has become a severe problem in Quebec and northeastern American forest regions in recent years due to several causal agents (McIlveen et al. 1989). In Ontario, assessment of maple decline has been conducted at 110 test plots by the Ontario Ministry of Environment since 1985. Individual trees are visually evaluated by field crews for evidence of decline symptoms such as chlorosis, undersized leaves and dead branches. This ground-based methodology is limited by: i) the subjectivity of visually estimating proportions of tree crowns exhibiting decline symptoms, and ii) by the nature of sugar maple decline which usually begins in the uppermost parts of the crown and progresses downwards.

An alternative to ground-based assessment is remote sensing which provides both a vertical view of tree crowns from above and digital image data which can be quantitatively and objectively analyzed. Decline symptoms are manifested in large scale airborne multispectral imagery in two ways: i) through changes in crown spectral reflectance (or image brightness) in the visible and near-IR regions of the spectrum, and ii) changes in crown texture (spatial variation of image brightness within each crown) due to changes in leaf orientation, proportion of shadows, exposed branches and background reflectance contributions. The principal limitation of remote sensing for decline assessment is that only dominant and co-dominant trees can be assessed.

Multispectral video imaging, a recently developed remote sensing technique, has proven to be useful in many forest applications using both analogue and digital image analysis methods (King and Vlcek 1990; King 1988; Yuan et al. 1987). In particular, large scale video can provide a close view of individual tree crowns at a fraction of the cost of multispectral scanning or ground surveys.

PREVIOUS RESULTS

In 1987, research was initiated to develop a video-based maple decline index which incorporates both image spectral and textural characteristics of individual tree crowns. The methodology and results were described in detail in Yuan et al. (1991) and Vlcek et al. (1989). Figure 1 shows an example of the variations in crown image brightness in four spectral bands for selected trees ranging from healthy to severely declining.

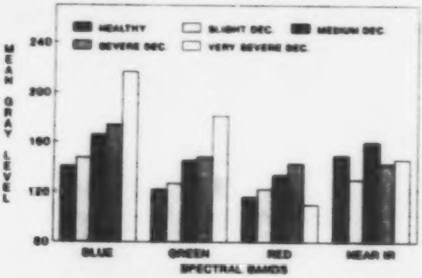

Figure 1. Spectral comparison of five maple trees.

Figure 2 shows an example of crown textural differences between a healthy (left) and declining (right) tree in the green band. The proportional increase in standard deviation of the pixel values is greater than the proportional increase in the mean brightness of the crown.

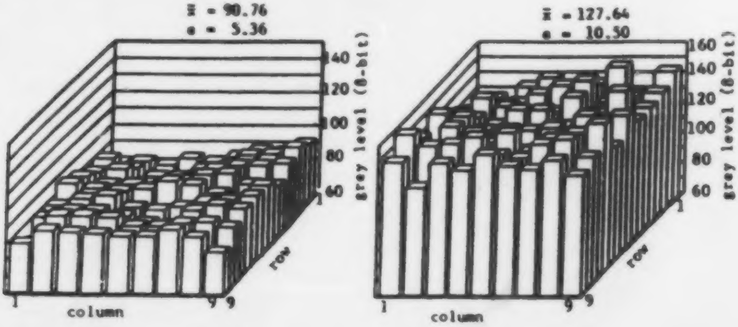

Figure 2. Spatial distribution of pixel grey levels in a 9x9 window of a healthy a severely declining tree crown in the 530-570 nm band.

In imagery of six MOE plots, several spectral and textural variables were evaluated for their relation to air photo-interpreted decline parameters. A linear model shown below (1) was proposed which included the second principal component in 4-band video imagery and a second order, co-occurrence matrix texture measure termed 'Contrast'. In the model, these measures are determined for each selected tree and compared to the same measures for a healthy reference tree nearby. The use of a healthy reference tree permits between plot comparisons since growing conditions for sugar maple vary from site to site.

$$DI = a_1 + a_2 S_d + a_3 T_d \qquad (1)$$

where: DI = decline index for a sampled tree

S_d = spectral distance between the sampled tree and the reference (healthy) tree

T_d = texture distance between the sampled tree and the reference (healthy) tree

a_1, a_2, a_3 = regression coefficients.

Comparison of the decline index with MOE ground-based index was only possible on a plot-by-plot basis because it was too difficult to match individual trees in the video images with numbered MOE trees at each site. However, a ranking of decline of the six plots matched very closely with the ranking of the MOE index. The objectives of this phase of the research are to: i) determine the best relationships between image parameters and ground decline index parameters using data from individual trees, ii) compare video-based individual tree decline assessments with MOE field assessments for relative accuracy and cost-effectiveness of the video method, and iii) refine the data acquisition and analysis methodology.

METHODOLOGY

Airborne data acquisition for decline assessment acquired in mid- to late August are presently being analyzed so results are not yet available. Consequently, the description below is of the preparation for, and acquisition of airborne multispectral videography.

Site selection

Four sites near Peterborough were selected based on decline and site data given in the 1986 to 1990 MOE sugar maple decline reports (McIlveen et al. 1989; Ecological Services for Planning Inc. 1989; Beak Consultants 1991). The principal criteria for site selection were that they had to: i) represent a range of decline levels from healthy ($DI < 11$) to poor ($DI > 20$), ii) have relatively stable decline indices during the last three years, iii) be situated fairly close to each other in the same physiographic region, iv) have similar soils characteristics (similar texture, good depth to carbonates and low stoniness) and slopes (being as close to flat as possible), and v) have been free from insect defoliation in the last three years.

Site Visits

Initial site visits were made in late June to evaluate the suitability of each for airborne remote sensing coverage. Tree crowns which would be visible to a camera system directly overhead were identified. Photographs of each suitable tree were taken to aid in tree identification in the video imagery. In addition, reference targets such as water, quarries and roads which were on the flight path for each site were identified. These will be used to normalize the data for varying illumination characteristics.

Flight preparation

Flight preparation included the following: i) acquisition of narrow bandwidth spectral filters (blue: 445-455nm, green: 545-555nm, red: 665-675nm and near infrared: (795-805nm)) based on literature review and previous experience, ii) rotational alignment of the four cameras in the camera mount, iii) determination of flight altitude (600m above ground level) for suitable resolution of individual tree crowns while minimizing image motion, and iv) layout of flight lines on 1:50,000 topographic maps for coverage of sites as well as reference targets. Flight lines were selected to be south to north following the road network to simplify aircraft navigation and minimize illumination-view angle variations across the images.

Data acquisition

The flight was conducted August 23, 1991 between 12:30 and 14:00 EST. Three sites were in full sun illumination. At each site a crew placed two red inflatable balloons beside pre-determined trees and monitored their position during flyover. The balloons were not visible from the air as had been hoped for navigational purposes. However, two sites were still completely covered by the videography and 35mm stereo photography which was acquired simultaneously. One site was partly covered and the other which was under cloud shadow was missed by about 20m. Beak Consultants of Brampton, Ontario (the current MOE contractor for decline assessment) evaluated the four sites within one day of flyover using the standard MOE decline index method.

Data Processing

The video data for each site and several reference targets were digitized at 512 x 480 pixel density using a frame grabber. This produced a digital image ground pixel size of 0.48m x 0.38m. The balloons are distinctly visible in the red band images and in the 35mm photos. Currently, enlargements of the 35mm photos for each site are being analyzed to determine the MOE numbers for individual trees and identification of the trees in the video images is being conducted.

Future Work

In the period of Oct. 1991 - Mar. 1992, the following will be conducted: i) normalization of data for different plots using reference target brightness distributions, iii) determination of the image spectral and textural measures within delineated windows in each tree crown, iv) decline index determination for each tree, iv) statistical comparison of image measures and decline index with the corresponding ground-based decline measures, and v) analysis of the accuracy and cost-effectiveness of the videography method relative to the ground-based method.

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BP2

UPTAKE, EFFECTS AND DISTRIBUTION OF NAPHTHALENE AND NAPHTHOL IN VEGETABLE PLANTS FOLLOWING FOLIAR AND ROOT EXPOSURE. B.A. Hale and D.P. Ormrod, Department of Horticultural Science, University of Guelph, Guelph, Ontario N1G 2W1.

The phytotoxicity and potential for contamination of vegetables by organic compounds of industrial origin is of increasing concern to members of both public and private sectors. While a considerable data base on the uptake and accumulation of agricultural organic chemicals by vegetation exists, thesimilar data base for industrial organic compounds is scanty. The information on agricultural chemicals cannot be readily transferred to industrial contaminants, as the molecular characteristics of the two groups of compounds are quite different. The uptake of organic compounds from soil or air by plants is dependent on numerous parameters, including the size and water solubility of the compound, and the tendency of the compound to adhere to soil particles. For the purposes of risk analysis, it is desirable to determine dose-response relationships describing the growth response to and tissue accumulation of organic pollutants, relative to various environmental parameters. This paper describes preliminary results of a study, the objectives of which are to relate foliar and root exposures of various vegetable species to naphthalene/naphthol, to growth and tissue concentration responses, as they relate to soil type.

Seeds were sown in either Promix BX (high cation exchange capacity), a mixture of sand and Promix BX (low cation exchange capacity) or a mixture of vermiculite and Promix BX (medium cation exchange capacity), at a rate of three seeds per pot. The pots were then placed in a controlled environment chamber which delivered a day/night temperature regime of 25/20°C, each for 12h, canopy level photosynthetically active radiation at 325 $\mu E\ m^{-2}s^{-1}$ for a 16h photoperiod and 70% relative humidity. Following covariate measurement, the plants were placed in exposure cubes with environmental conditions similar to those in the controlled environment growth chambers. Two ml of naphthol or naphthalene in ethanol were applied to the soil; plants were harvested on the third day after application of the contaminant. Foliar injury, as well as fresh and dry weights of shoot (divided into stem, leaf and hypocotyl where applicable) and leaf area were assessed on the plants. Exposure of shoots to air containing naphthalene was accomplished by constructing large permeation tubes through which air was passed and then metered into the main air stream entering the exposure chambers. Alteration of the rate of air flow through the permeation tube with a flowmeter controlled the concentration of naphthalene in the chamber. Determination of exposure concentration was by gas chromatography, using manual injection; samples were taken hourly during the five days of exposure. At the end of the exposure, analysis of naphthalene concentration in plant tissues was determined; since the tissue was not washed prior to analysis, the values represent surface adsorption as well as absorption. The experimental design for the soil exposure was a partial central composite, with seven contaminant concentration/soil CEC combinations. The central treatment (CEC=med, naphthol/naphthalene concentration=10 mg/l) is repeated twice for each replication of the other points, in order that all areas of the response surface have approximately equal estimates of variance. The treatment means were summarized by polynomial functions in the second order for both factors, including an interaction term.

The growth of radish, tomato and swiss chard declined in response to naphthol applied to the soil, but the severity of the growth reduction was more closely related to the cation exchange capacity (CEC) of the soil than to the concentration of the contaminant (data not shown). It is known that soils with a higher CEC tend to make organic contaminants less available for plant uptake, thus reducing the phytotoxicity of the contaminant. Tissue accumulation of naphthalene (similarin composition to naphthol) following soil application was determined, as well as the actual concentration in the soil at the time of plant harvest. The results of the soil analysis confirmed the conclusion of the previous experiment, that at higher soil CEC, more naphthalene was retained by the soil likely reducing availability to plant roots. As well, as applied concentration increased, so did soil concentration of naphthalene. Tissue concentration of naphthalene following soil exposure was highly variable, with very weak trends towards increasing with applied concentration and decreasing with higher CEC (Table 1). It is not clear at this point whether the variability truly represents that found in plant response, or whether the analytical process for the detection of naphthalene in tissue is highly variable. It is possible that much more replication is needed to detect differences among treatments.

Tissue concentrations of naphthalene from the first replication of the experiment in which the plant shoot was exposed to atmospheres containing various concentrations of naphthalene, demonstrated no consistent effect of soil type, but were related to exposure concentration and species (Table II). Tomato shoot had the highest tissue concentrations of naphthalene at all exposure concentrations, while the other two shoot types had similar tissue concentrations, relative to exposure concentration. Radish root data were similar to that for radish shoot. When plant shoots were exposed to atmospheres containing naphthalene, tissue concentration was independent of soil type, as could be expected. However, it was related to exposure concentration and plant species; this latter factor probably relates to the affinity of the leaf surface for the compound (i.e. the presence of trichomes or cuticular waxes). It is clear from these data that greater separation of treatment concentrations is required for the establishment of dose-response relationships.

Future work includes further investigation of tissue accumulation following foliar exposure, with particular emphasis on investigating ways to better control the concentration of volatilized compound in the air. In addition, integration of all of the data into a single model relating phytotoxicity and the experimental parameters will be investigated.

TABLE I: Treatment means for tissue and soil concentration of naphthalene for tomato grown in three rooting media differing in CEC and applied concentration of naphthalene.

Analysis	Solution Concentration (mg/l)				
Soil Type	.10	1.0	10	100	1000
Tomato leaves					
P + S	n.a.	.078	n.a.	.085	n.a.
P + V	.073	n.a.	.073	n.a.	.43
P	n.a.	.060	n.a.	.063	n.a.
Soil at harvest					
P + S	n.a.	.09	n.a.	.950	n.a.
P + V	.50	n.a.	1.10	n.a.	188
P	n.a.	3.41	n.a.	26.0	n.a.

P + S indicates Promix/sand mixture;
P + V indicates Promix/vermiculite mixture;
P indicates Promix used alone;
n.a. indicates not available

TABLE II: Treatment means for tissue concentration of tomato, radish and swiss chard grown in media with different CEC's and exposed via the atmosphere to various concentrations of naphthalene.

Species		Exposure Concentration (ng/cc)			
	Soil Type	12	14	19	65
Swiss Chard shoot					
	P + S	.03	.01	.03	.16
	P + V	.02	.02	n.d.	.11
	P	.06	.06	.04	.18
Tomato shoot					
	P + S	.48	.26	n.a.	2.20
	P + V	.42	.25	.16	2.30
	P	.14	.22	.21	1.10
Radish shoot					
	P + S	.09	.03	.03	.16
	P + V	.04	.03	.21	.30
	P	.05	.03	.05	.30
Radish hypocotyl					
	P + S	.02	.01	.02	.10
	P + V	.02	n.d.	.02	.11
	P	.05	n.d.	n.d.	.13

P + S indicates Promix/sand mixture;
P + V indicates Promix/vermiculite mixture;
P indicates Promix used alone;
n.d. indicates below limit of detection;
n.a. indicates not available

BP3

BIOMAGNIFICATION OF COPLANAR POLYCHLORINATED BIPHENYLS. Susan Koslowski*, Biological Sciences, University of Windsor, Windsor, Ontario, N9B 3P4 and G. Douglas Haffner, Great Lakes Institute, University of Windsor, Windsor, Ontario, N9B 3P4.

Despite the restriction of import, manufacture and use of PCBs in Canada in 1977, the global ecosystem is still plagued by these pollutants.

Traditionally, organochlorine contamination has been evaluated by total PCB content; however, recent advances in sample clean-up and GC programming have facilitated the identification of numerous individual congeners. Research indicates that toxic potential related to the presence of non-ortho and mono-ortho substituted tetrachlorodibenzo-p-dioxin, and thus possess the ability to induce the mixed function oxidase system (MFO), and specifically, the enzyme aryl hydrocarbon hydroxylase (AHH).

Sampling of a wide range of biota in the western basin of Lake Erie during the summer of 1991 was performed to quantify coplanar PCB dynamics through the trophic levels of a freshwater foodweb. Coplanar PCB were found at concentrations as high as 9.3 ug/kg in gull eggs, and 2.5 ug/kg in suckers, while lower trophic levels exhibited reduced body burdens which were often non-detectable. To further quantify the coplanar PCB environment via biomagnification, extractions from species of various trophic levels will be used to induce AHH activity in the HII4E rat hepatoma cell line.

[illegible]

LIFE HISTORY AND DEMOGRAPHICS OF THE ZEBRA MUSSEL (*DREISSENA POLYMORPHA)* IN LAKE ST. CLAIR.

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The zebra mussel, *Dreissena polymorpha*, was introduced into the Great Lakes probably in the fall of 1985, from the ballast water of freighters originating in Europe. They were first discovered in Lake St. Clair in June of 1988 and are now found throughout the Great Lakes. The life history and demographics of the zebra mussel population at Puce, Ontario, along the southwest shore of Lake St. Clair has been studied, and comparisons made to other populations in the Great Lakes and Europe. Adult zebra mussels from the Puce area have a life span of about 2.5 years and rapid growth rates of up to 2.0 cm per year. Maximum shell lengths average 2.3 - 2.5 cm, with standing crops now exceeding 200,000 m^{-2}. Fertilization is external and veligers appear to require 3 - 5 weeks before settlement occurs. In 1990 the first appearance of free swimming veliger larvae at Puce was observed June 20 at a water temperature of 21°C but in 1991 larvae first appeared mid May at 15°C. In 1990 veliger numbers peaked the first week of July at 162,000 m^{-3} and disappeared from the water by mid October. One peak in veliger abundance occurred in 1990 while two peaks occurred in 1989. Within Lake St. Clair there are annual variations in the time of first appearance of larvae, number of peaks per year, abundance and settling periods.

BP6

RESPONSE OF SUGAR MAPLE, RED SPRUCE, NORWAY SPRUCE, AND BALSAM FIR SEEDLINGS TO ALUMINUM STRESS AND PHOSPHORUS DEFICIENCY.

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The purpose of this study is: (1) to compare relative Al tolerance of *Acer saccharum*, *Picea rubens*, *Picea abies*, and *Abies balsamea* seedlings, (2) to determine degree to which Al-tolerant plants are able to exclude Al and to take up Ca, P, and trace nutrients in the presence of Al, and (3) to investigate possible mechanisms of Al tolerance including the ability of plants (i) to increase rhizosphere pH and thus precipitate Al, (ii) to release organic acids and thus chelate Al, and (iii) to produce acid phosphatase during periods of P deficiency.

Seedlings were grown hydroponically for 4 to 6 days in a modified Ingestadt nutrient solution at pH 4.0 with (10 mg/L) and without Al and with (10 mg/L) and without P.

Red Spruce was the most Al-sensitive species tested based on our criteria. It did not increase rhizosphere pH, release citric acid, or produce acid phosphatase when exposed to elevated concentrations of Al or to limiting concentrations of P (Fig. 1). When exposed to Al it had lower concentrations of Ca, Cu, and Zn in the roots and higher concentrations of Al in both the roots and the shoots. Aluminum concentrations increased almost three fold in the shoot and ten fold in the root (Fig. 2).

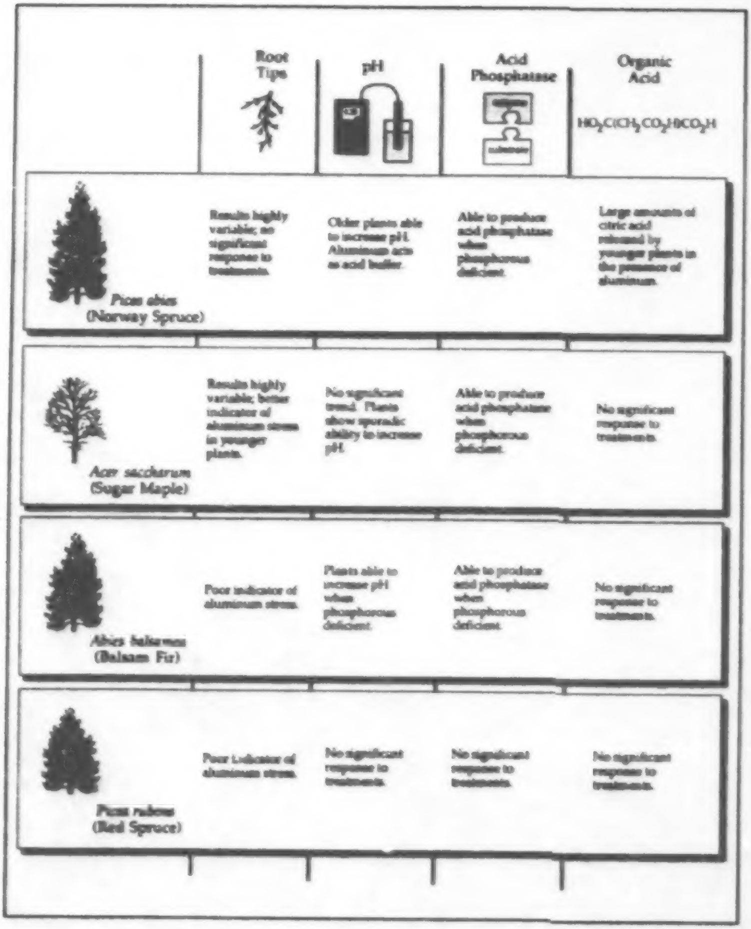
Balsam Fir was the second most Al-sensitive species. It produced acid phosphatase and increased solution pH when P-limited, but did not overcome the acid-buffering when Al was present nor did it release organic acids to chelate Al (Fig. 1). Aluminum appeared to interfere with the uptake of Ca, Mg, Cu, Mn, and Zn in the roots. No significant amount of Al was translocated to the shoot but root concentrations increased three and a half fold (Fig. 2).

The two populations of **Sugar Maple** differed in their Al-sensitivity. Sugar Maple did not increase rhizosphere pH or produce organic acids, but did produce acid phosphatase when P-limited (Fig. 1). Aluminum was translocated to the shoot (Fig. 2) and interfered with Cu, Mn, and Zn in the root.

Norway Spruce was the least Al-sensitive species tested, but once again the populations differed in their response. One population produced acid phosphatase when P-limited, the other suppressed enzyme activity when Al was present (Fig. 1). Aluminum interfered with uptake of Ca, Cu, and Zn in roots of both populations and was translocated to the shoot in one population. Aluminum concentrations in the roots increased five fold.

Root growth, expressed as the number of new rooting tips, has been successfully used to rank Al-sensitivity of wheat seedlings. However, neither this measure of root growth nor changes in root length were reliable indicators of Al stress in tree seedlings due to the high variability among individual plants (Fig. 1). Clonal material and a longer experiment may give more reliable results.

Phosphorus concentrations were significantly higher ($P=0.05$) in the root but not in the shoot of Balsam Fir, Norway Spruce, and Red Spruce exposed to elevated Al concentrations (Fig. 3). Aluminum and P concentrations were positively correlated in the roots of Red Spruce and Balsam Fir, and one population of both Sugar Maple and Norway Spruce. These results suggests that Al and P may be chemically complexed and may not be bioavailable despite the elevated concentrations found in the roots.



	Root Tips	pH	Acid Phosphatase	Organic Acid $HO_2C(CH_2CO_2H)CO_2H$
Picea abies (Norway Spruce)	Results highly variable; no significant response to treatments.	Older plants able to increase pH. Aluminum acts as acid buffer.	Able to produce acid phosphatase when phosphorous deficient.	Large amounts of citric acid released by younger plants in the presence of aluminum.
Acer saccharum (Sugar Maple)	Results highly variable; better indicator of aluminum stress in younger plants.	No significant trend. Plants show sporadic ability to increase pH.	Able to produce acid phosphatase when phosphorous deficient.	No significant response to treatments.
Abies balsamea (Balsam Fir)	Poor indicator of aluminum stress.	Plants able to increase pH when phosphorous deficient.	Able to produce acid phosphatase when phosphorous deficient.	No significant response to treatments.
Picea rubens (Red Spruce)	Poor indicator of aluminum stress.	No significant response to treatments.	No significant response to treatments.	No significant response to treatments.

Figure 1. Response of tree seedlings to elevated concentrations of Al and limiting concentrations of P.

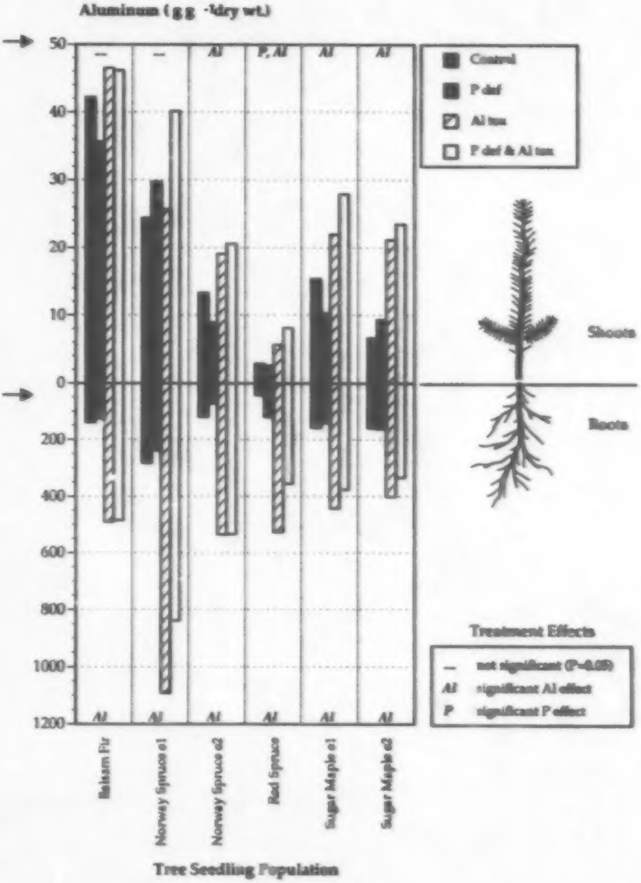


Figure 2. Aluminum concentrations in the root and shoot of tree seedlings exposed to elevated concentrations of Al and limiting concentrations of P.

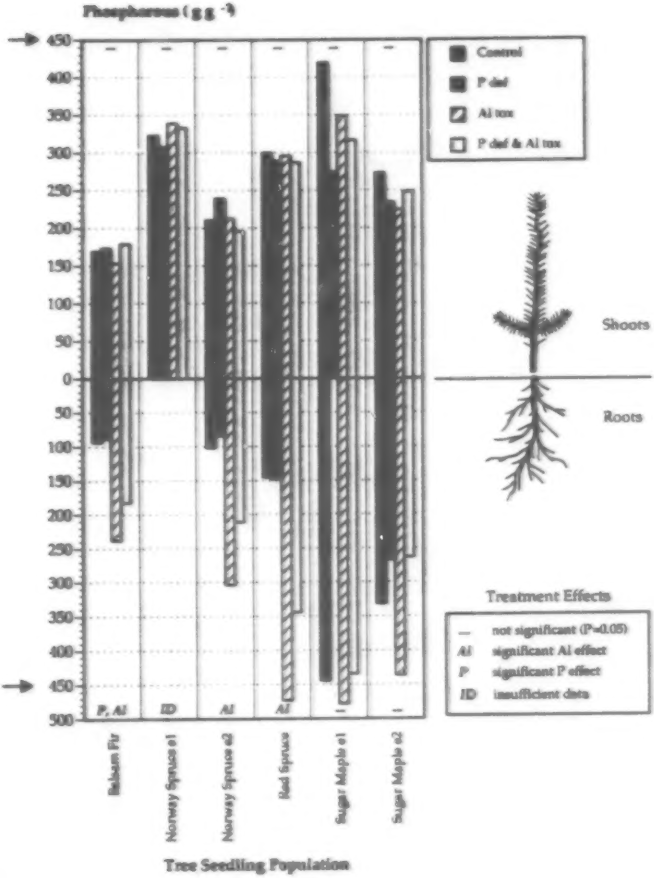


Figure 3. Phosphorous concentrations in the root and shoot of tree seedlings exposed to elevated concentrations of Al and limiting concentrations of P.

VOLUME I

SESSION C

ENVIRONMENTAL MANAGEMENT OPTIONS

VERBAL PRESENTATIONS

C1

Economy-Environment Linkages:
Sustainable Development in Ontario

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Paper Presented at the Technology Transfer Conference, 25 November, 1991

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1. Introduction

The main objective of this research project is to develop a framework that will:

- provide a means of quantifying economy-environment linkages in Ontario;
- assist the examination of sustainability of development in Ontario through scenario analysis;

A secondary objective is to help generate a sound basis for a set of integrated provincial economy-environment accounts. Furthermore, the groundwork will be laid for the extension of the framework in the future to include a model of one or more renewable resources in Ontario.

Subsequent to the approval by the Ministry of the Environment of the project proposal, a third component was added:

- to develop and implement a procedure which estimates the residuals discharged from sewage treatment plants.

The project was initiated in July 1990 and is being conducted by a joint team of economists and environmental scientists from VHB and ERL. A multi-disciplinary group from federal and provincial government departments and Universities has been established to provide advice to the project team.

This paper highlights several aspects of the project including the interpretation of sustainable development as development that respects bio-physical and socio-economic constraints, the theoretical model that has been created, and the economics and environmental data that has been assembled to implement the model. Planned applications of the model are noted but specific results will not be available until the completion of the project in early 1992.

The Meaning of Sustainable Development

The approach taken in this research project to the meaning of sustainable development starts from a pre-analytic vision of the economy as a sub-system of the ecosphere. The economy consists of the activities commonly referred to as production, distribution and consumption undertaken by humans. Not only is the economy a sub-system of the ecosphere; it is also a sub-system of the larger set of activities that make up social life.

The economic sub-system is connected to the ecosphere in three main ways:

- the materials and energy required by the economy are obtained from the ecosphere;
- the waste materials and energy no longer required by the economy are returned to the ecosphere;
- economic activity takes place in the space provided by the ecosphere.

Seen in this light, the economy is an open system through which materials and energy flow from and to the ecosphere. This view of an economy may be contrasted with the more conventional picture given in most introductory textbooks on economics where it is shown as two concentric circular flows with incomes and expenditures going in one direction and goods and services going in the other: a perpetual motion machine with no apparent connection to the ecosphere; an economy with no environment.

As the scale of economic activity has increased so have the demands placed on the environment for resources, waste disposal and space. One policy response to these increasing demands has been for governments to impose absolute limits on the flows to and from the environment and also on the use of space. This increasing reliance on absolute limits to protect the environment gives an important clue to the meaning of sustainable development.

To a large extent, the concern that development is not sustainable stems from a combination of i) concern that certain trends projected into the not too distant future cannot be sustained, and ii) a belief that the economic system cannot be relied upon to make the necessary adjustments without some form of government intervention. It follows that if development is not sustainable because certain limits are not being respected, then sustainable development requires that economies operate within such limits. The market system can continue to function but it must be obliged to do so by operating within limits imposed by government in order to avoid the uncertain consequences that nature herself will ultimately impose.

From a modelling perspective, the concept of limits can be introduced through a set of constraints expressed mathematically. More problematic is the selection of the variables that should be constrained to capture the meaning of sustainable development and the measurement of such variables. The challenge is to specify a set of constraints that are comprehensive and measurable without becoming too detailed.

The approach adopted in this project to defining a set of sustainability constraints is to start with six primary biophysical constraints: water, air, minerals, solar radiation, surface area, and genetic material. The supply of water, air, minerals and natural genetic material can be expressed in terms of both quantity and quality. In addition, various combinations of these factors lead to significant foundations for biological production and economic activity. For example, agricultural soil requires certain specific supplies of minerals and surface area. Similarly, climate is a function of solar radiation and air quality.

The total quantity of each of these six constraints is for all practical purposes fixed. The quality of the supply is highly variable and subject to human influence. Substitution among the constrained factors is also variable and often extremely complicated. For example, the amount and quality of agricultural land may be a primary indicator of sustainable development. Through technology and energy inputs, losses in supply due to urban expansion may be compensated by improvements in the quality of the remaining agricultural land. However, such compensation is not unlimited since the available surface area is fixed. Only by maintaining a careful accounting of the primary constraints will these limits be revealed.

In general, to quantify the constraints that define sustainable development, data are required with respect to:

- the total current supply in quantity and quality terms of each primary constraint;
- the combinations of primary constraints that lead to the direct connections with the economy (e.g. agricultural land produces agricultural goods accounted for in the economic framework);
- the production coefficients for primary renewable and non-renewable resources with various combinations of primary constraints;
- the waste emission coefficients from various forms of economic activity;
- the relationships between the waste emissions and the productive capacity of the environment.

A major component of current activities is the reconciliation of the ideal information requirements of the constraints with available data. Concurrently, the expression of the constraints and their relationships are being developed in a form consistent with the economic component of the model framework. The biophysical response models are not at this time being included, however, efforts are being made to ensure that essential connections are possible.

To apply this approach to a sub-region such as Ontario it is also necessary to impose limits on Ontario's imports and exports of traded goods and services. Over the long term, it is inconsistent with sustainable development for Ontario to maintain an increasing net trade deficit with the rest of the world. Therefore, another component of the meaning of sustainable development in Ontario is that the value of imports and exports with the rest of the world be equal and a constraint can be imposed to that effect.

The Analytical Model

The core of the analytical model is input-output analysis and the main source of economic data for estimating the model is Statistics Canada. Several economists, including one of the members of the project team (Victor), have shown how conventional input-output models of the economy can be extended to include the flows of materials and energy from and to the environment. Taking advantage of the high level of disaggregation input-output models offer, these linkages to the environment can be specified for each of numerous sectors.

A further dimension of the project is that it utilizes an approach developed by another member of the project team (Kubursi) that integrates location theory with input-output analysis so that the model estimates economic activity and impacts at the sub-provincial level. In fact, by geocoding the economic data base from which the input-output model is estimated, it is possible to assign economic activity by sector to any geographic representation of the province that the geocoded information allows. For example, in this project the model is being configured by county and by watershed.

In addition to the material and energy flows (expressed as coefficients of tonnes of material per dollar of activity), the model incorporates business investment and consumer expenditures as endogenous functions. More significantly, extensive work has been undertaken to include alternative production technologies in the pulp and paper sector as well as a waste management sector that provides services to business, households and government. Recycled materials are explicitly included as are a variety of products that are manufactured from them.

Finally, as a spin-off, new work has been undertaken on the treatment of non-renewable resources within the system of national and provincial accounts to assign a portion of the net returns from the sale of minerals to capital depletion rather than treating it all as income as in the conventional practice.

The Environmental Data Base

In order to model the interaction between the economy and the environment, detailed information on the resources used and wastes generated by each form of economic activity is required. Furthermore, quantitative and qualitative information on the current supply of resources is needed to quantify the constraints which define sustainable development. An important component of this project has been the collection of these data for the province of Ontario.

The environmental data base is comprised of three separate data bases: the resource use, waste generation and resources at risk data bases. The topics covered by each data base are listed below:

resource use	**waste generation**	**resources at risk**
mining	emissions to air	population
forestry	emissions to water	forest stands
agriculture	emissions to land	agricultural lands
fisheries		surface water
water use		ground water
		endangered plants and animals
		buildings and materials

The data in the environmental data base have been compiled using 4 digit SIC codes and two separate spatial formats: counties and sub-sub watershed basins. County boundaries are suitable lines along which to organize data in order to analyze linkages between the economy and the environment such as emissions to air, the production and disposal of hazardous and municipal waste, the extraction of minerals and exploitation of renewable resources such as forests and fish. However, to relate economic activity to factors such as water use, erosion, and the discharge of residuals into Ontario's lakes and rivers it is advantageous to organize data according to watershed basin boundaries. All of the data in the Environmental data base are being converted to latitude and longitude for incorporation in a GIS system to increase the flexibility of the system.

Significant quantities of data have been collected in virtually every area targeted by the project team. Furthermore, virtually all of the information contained in the EDB dates from the period between 1985 and 1989.

Despite the overall success of this component of the project, there are shortcomings in the environmental data base. These tend to fall into two categories. First of all, it has not always been possible to obtain suitable data for the 1985 - 1989 period, to correspond directly with the economic data. Consequently there are many areas of the data base in which data are only available for one or two years of this period. This may present a problem when calibrating the model for different years. Secondly, in some cases gaps exist because of restrictions on dissemination of the information to protect the confidentiality of reporting companies.

Model Implementation

By combining the economic data and the environmental data, material and energy use and disposal coefficients are being estimated. In cases where alternative technologies are recognised, these coefficients will be technology specific rather than sector specific. In any case, the high degree of spatial disaggregation allows for different technologies to be used by sectors according to their location.

Several issues are being addressed to illustrate the model's utility:

i) Constraints will be imposed on the model to define sustainable development for Ontario. The implications of these constraints for economic development in the Province will be explored. Of particular interest are the regional and sectoral implications on employment, production, value added, trade and taxes of a requirement that the stock of capital and natural wealth be maintained for future generations.

ii) For any constraint that is binding, a 'shadow price' will be estimated that shows how gross provincial product will change for a small change in the level of the constraint. These shadow prices will serve as an interesting indicator of the relative economic significance of each of the individual constraints.

iii) The shadow prices will be incorporated into a set of price equations the solution to which will show the 'full cost' of each commodity in the economic model. These calculated prices that reflect conditions for sustainability will be compared with market prices for each commodity.

iv) The potential role of substitution and technical change in sustainable development will be explored by focusing on one or more sectors (pulp and paper and possibly agriculture) where information on alternative processes is being assembled.

MULTI-MEDIA EXAMPLES IN ENVIRONMENTAL MANAGEMENT APPROACHES

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Introduction

The OECD defines the term "multi-media" as referring to approaches to environmental management that consider the problems occurring when chemical substances are released from a single source to more than one environmental medium (air, land or water) and when a target receptor is exposed to chemical substances via more than one carrier (air, water). In the following discussion multi-media is also referred to as "media-integrated", recognizing this form of integration as a subset of the broader area of integrated pollution control.

The research described in this presentation forms part of a project for the Ministry of the Environment to critically examine multi-media approaches in other jurisdictions, to review multi-media issues in Ontario, and to propose potential case studies to further understanding of the application of a multi-media approach in Ontario.

Definition of Terms

In order to discuss the approaches taken in different jurisdictions, it is first necessary to develop a framework of terminology. The following are the key terms used here in discussing environmental management programs.

Integrated Pollution Control

> is used in two senses; "internal" integration, referring to linking air, water and waste programs to reduce total risk to the environment; and "external" integration, referring to integration between environmental policy and other policy sectors such as energy and agriculture.

This discussion emphasizes the first of these, which is assumed to inherently involve a multi-media approach.

Source Reduction

> is any practice which reduces the amount of any hazardous substance entering any waste stream or that is otherwise released into the environment (including fugitive emissions) and reduces the hazards to the public health and environment associated with the release of such substances.

In this discussion, source reduction is included in the more general category of preventative approaches, also used to describe approaches that include pollution prevention, waste reduction and/or waste minimization (depending on the definitions applied).

Ecosystem Management

> is the setting of quality and emission control targets and objectives based on the aggregate impacts of different pollutants and physical intrusions on the surrounding receptors within a natural geographic area.

Discussion here of ecosystemic approaches is limited to the context of managing pollutants.

Analysis Criteria

This review focuses on the results, rather than intents, of programs. As such, the first consideration in examining jurisdictions was to what extent programs had been implemented, and how much evaluation of program impacts had been carried out. The general evaluative criteria sought were:

- the economic efficiency of the program, in terms of overall costs and benefits;
- the environmental effectiveness of the program, in terms of contamination and impact reduction; and
- the equity of the program, in terms of the distribution of costs and benefits among sectors of society.

In the absence of rigorous evaluative data on benefits achieved, several other screening criteria were used in the data gathering stage. The concept of a successful program was defined by:

- degree versus duration of implementation (measured against the intended scope of the program);

- number of groups involved in implementation and ongoing operation of the program (with the assumption that broad involvement reflects positive evaluation); and
- program activities being carried to a practical level.

Program Identification

An initial survey identified 25 jurisdictions as having or developing programs related to the multi-media approach. These included the US EPA and seventeen state programs, the EEC and five European countries, and two Canadian provinces.

The programs identified were grouped into the following categories:

- multi-media approaches in conventional management, including integrated permitting, enforcement etc. (these generally have an "end-of-pipe" focus);
- preventative initiatives that involve a multi-media approach; and
- ecosystem based approaches, accounting for the total impact from all sources within a natural geographic area.

Most programs identified in North American jurisdictions involve some type of pollution reduction approach (toxics use reduction, waste minimization, hazardous waste reduction). Many of these programs are non-regulatory, using provision of technical assistance or other means to encourage voluntary participation. They generally involved the creation of new government departments or groups, with very little reorganization of existing structures. Multi-media is an element (or by-product) of these programs and as such is implemented at operating levels as part of polices rather than as a policy in itself.

The European programs are based more on the permitting process and development of the process to account for cross-media issues. European governments displayed a tendency to reorganize existing bodies and structures. In the UK this is probably part of a policy of "minimum government" where fiscal restraint has discouraged the creation of new government agencies. In European jurisdictions, multi-media has been taken as a goal in itself; the benefit of overall optimization has been deemed worthwhile even without source reduction targets or mandates.

In spite of the different role multi-media is playing in environmental management in Europe and North America, there were a number of similarities observed with respect to the management programs studied. All successful programs either incorporated or recognized a future need for a multi-media approach to pollution prevention. Most of the programs were initiated on the basis of a general belief that effective environmental management relies on some sort of integrated approach, and none of the programs was preceded by in depth economic analysis, although all programs acknowledged the economic impacts.

Another area of commonality was in concerns expressed by participants which they felt needed to, and could, be addressed by the programs:

- sub-optimization in industrial design from a combination of environmental protection and economic viewpoints, including the need for cost effective alternatives to enormous cost of treating and controlling wastes under existing approaches;
- cross-media transfers and multi-media impacts; and
- pollution from non-point sources.

Additional concerns were common from a focused business and economic standpoint:

- costs associated with liability and clean-ups, and
- increase of "NIMBY" (not in my back yard) attitude to waste disposal.

The following factors were found to be common to the success of multi-media environmental management programs in different jurisdictions:

- provision for public access to information;
- development of a database on the use and release of toxic materials;
- requirement that emitters inform regulating bodies of toxic releases to the environment;
- development of a close relationship between government and industry in defining the means (not necessarily the goals) of administering the environmental programs; and
- availability of technical assistance.

Critical Analysis

Four jurisdictions were selected for more in depth analysis:

- the Blackstone Project and Toxics Use Reduction Act (TURA), Massachusetts, US;
- the US EPA Yorktown project, Yorktown, Virginia;
- in the United Kingdom, the Integrated Pollution Control and integrated inspection programs; and
- in Germany, the integrated permitting approach in Hamburg.

Two additional jurisdictions, Sweden and the province of Quebec, were determined to have noteworthy programs.

Sweden

Although not pursued in detail, the Swedish permitting system represents an approach that is clearly multi-media and apparently effective from an administrative stand-point. In Sweden, all permits for major industrial and municipal installations are approved by a single national body, the Franchise Board. Permits for smaller (or less polluting) installations are approved at the county or municipal level, again by single boards. Decisions of the boards are based on overall pollution levels from the particular installation. The national boards are made up of a chairperson, a senior engineer, a representative from the National Environmental Protection Board and a representative from the appropriate industry.

Although there are emission guidelines, Sweden does not have binding emission or environmental quality standards for most pollutants. Decisions on controls required at specific installations are based primarily on selection of Best Available Technologies. Permits are granted for the life of the plant. Although there is some scope to re-examine specific discharge levels after a permit is granted, applications for expansion or process changes are usually taken as the opportunity to re-examine overall discharge levels.

Although there is limited evaluation of the overall effectiveness of the approach, the fact that the system has been operating for some twenty years with no movement to change it's media-integrated approach provides strong evidence of the potential efficiency and effectiveness of a multi-media approach.

Quebec

One of the best examples of a multi-media initiative in Canada is the Quebec Programme de Réduction des Rejets Industriels (PRRI). The objective of this program is to reduce the aggregate volume of industrial waste by 75% over 10 years, focusing on toxic substances. The basis of the program is to be an "Attestation d'Assainissement", an overall waste stream reduction plan developed by each industrial establishment and approved by the regulatory authorities. The program takes an integrated approach to all waste streams.

The legislative framework for PRRI was included in Bill 99, however no regulations had been developed as of the summer of 1991. Five major industrial companies have been asked to take part in a trial program of waste characterization (beginning with water and soil) on a voluntary basis, however this program is proceeding very slowly.

Blackstone Project and Toxics Use Reduction Act (TURA) (Massachusetts)

The Blackstone project is a pilot demonstration project which was developed under the Massachusetts Departments of Environmental Protection (DEP) and Environmental Management (DEM). It incorporates legislation from the Toxics Use Reduction Act (TURA) of 1989 as applied to a subset of the state's industry. The program consists of coordinated multi-media compliance, inspections of industrial facilities, enforcement (with emphasis on source reduction) and coordination of regulatory and technical assistance activities.

The initial development of the legislation was by an environmental organization called the Massachusetts Public Interest Research Group, or Mass PIRG. Subsequent work was conducted by a team of representatives from industry, environmental groups and the Massachusetts government leading to the legislation passed in 1989. Justification for the projects came from a growing awareness of the inadequacies of a single-media approach to environmental protection (the problems of multi- and cross-media contamination), development of toxics release inventories indicating the volume of contaminants being released to the environment, escalating costs of disposal and clean-up operations, and increasing public pressure.

The purpose of TURA was to focus the attention of environmental protection efforts away from the traditional "end-of-pipe" method of pollution control, to the industrial "front-end" or the use of toxic and hazardous chemicals. The goal of the legislation, considered the foremost pollution prevention statute in the United States, was to achieve a 50% reduction in the industrial usage of toxic and hazardous chemicals. In particular, TURA requires the DEP to achieve the following by January 1st, 1992:

- to ensure, where appropriate, that facility inspections are multi-media in approach;
- that teams of inspectors should represent existing programs within the department; and
- that duplication of inspection and enforcement efforts should be minimized between departments and agencies.

The DEP is also responsible for:

- coordination of chemical use, release and disposal reporting; and
- coordination of toxics use reduction efforts within and between state agencies.

TURA is aimed at all industrial users of toxic and hazardous chemicals. While destined for state-wide application, Blackstone was limited to the metal industries within the service area of the Upper Blackstone Water Pollution Abatement District Sewage Treatment Plant in its 1990 fiscal year. Industrial users are subdivided as either large or small quantity users (LQU's and SQU's) where the former are defined as processing more than 25,000 lbs. or using more than 10,000 lbs. of a regulated substance, and the latter as processing or using less than the indicated amounts. Funding for the project is primarily provided through annual filing fees (toxics users registration) which each facility must pay based on the number of toxic substances reported and the number of employees.

TURA uses a broad definition of the term multi-media, including, but not limited to, water, land, air, and workplaces within facilities. Regulated substances are defined by the existing SARA (Superfund Amendment and Re-authorization Act) toxic chemical list. The legislation includes an amendment process which will allow for the addition and removal of substances from the list after 1994.

TURA requires the following of LQU's and SQU's in priority sectors:

- to develop and file toxic use reduction plans by 1994 (open to public inspection);
- manufacturing LQU's must file annual reports on substance use and release (open to public inspection); and
- non-compliers under the enforcement jurisdiction of the DEP must use toxics use reduction to achieve compliance.

A special feature of the program in Massachusetts, is the commitment to technical assistance. One initiative of TURA was the establishment of the Office of Technical Assistance (OTA) which provides help to industry in the areas of on-site evaluation of source reduction opportunities, economic analysis and information dissemination. Along the same line, the DEP, in cooperation with a state university, founded the Toxics Use Reduction Institute (TURI). The institute will focus on curriculum development for TUR inspectors, planners, consultants, and conduct research into TUR technologies, public education and policy development.

The DEP itself underwent significant changes in putting the new legislation into operation. The DEP was reorganized into several bureaus (one of which was the multi-media oriented Bureau of Waste Prevention), and all programs involved in regulating industry were brought under the auspices of the DEP. The single-medium divisions remained intact but whereas they operated independently of one another in the past, TURA will coordinate their efforts to achieve a multi-media policy direction. While established by the DEP, the OTA is independent of the DEP, thereby separating regulatory tasks and technical assistance. It was believed that this separation would encourage a more cooperative attitude with industry.

It is too early to be able to observe any environmental impacts produced by TURA and the Blackstone project, however positive feedback was received from many participants and observers. Mass PIRG was of the opinion that the process of preparing TURA reports would have a significant effect on industry in shifting their attention to source reduction. They also believed the debates in developing the legislation would lead to better data bases and more effective departmental coordination. The Blackstone models achieved as good or better results in achieving regulatory compliance and were considerably more effective in detecting illegal or unregistered waste streams. Participating industrial facilities were solidly behind the concept of multi-media inspections. More information will be available through the second annual report on the project in late fall of this year.

US EPA - Yorktown Demonstration

This pilot pollution prevention project is administered by the US Environmental Protection Agency (EPA). It is a joint effort between the EPA's Office of Policy, Planning and Evaluation and Amoco Corporation, and centred around Amoco's Yorktown, Virginia refinery. The idea for the program was originally proposed by Amoco to the EPA in November 1989 and was finally approved in March of 1990.

The project was designed to assess opportunities, benefits and obstacles in coordinated and concurrent permitting, to devise facility-wide strategies, options and management approaches for multi-media pollution prevention and reduction, and to promote education regarding refinery and regulatory systems. The goals of the study were defined as:

- to develop methods and approaches for facility-wide analysis of releases;
- to define and prioritize source reduction, recycling, end-of-pipe controls and environmental results; and
- to identify how the framework might be applicable to other facilities.

The study was divided into two parts. The first phase was the production of a release inventory of Yorktown refinery (completed early 1991 - Note: this study concentrated on release data while the Blackstone project collected data on contaminant use as well). Phase two of the project is the analysis and evaluation of the collected data (scheduled for completion in October 1991). While the study centred on one facility, the application is potentially for all industry and in particular the Petroleum Refining "Regulatory Cluster" (ie. industrial sector). All media were considered in producing the release inventory and the contaminants of concern were defined as those recorded under SARA 313 with the additions of NO_x, SO_x and CO. Since the workgroup had no authority to grant waivers to existing regulations, multi-media permitting and other prevention/reduction options were not utilised.

While no specific analysis occurred prior to the demonstration, numerous EPA reports provided justification for the work. Reports consistently identified weaknesses of existing pollution control directed incentives such as:

- perpetuating a "toxics shell game" (cross-media transfer) often at great expense with little or no environmental or human benefit; and
- failing to account for accumulative environmental impact from one or more sources and pathways.

Impacts to date are again difficult to measure, however, project leaders have suggested that the results should encourage consideration of restructuring the approach to environmental protection and provide an initiative to develop further strategies to efficiently achieve environmental benefits.

United Kingdom - Integrated Permitting and Integrated Pollution Control

In 1976, a Royal Commission on Environmental Pollution proposed directing contaminant releases to the medium which result in the least damage to the environment and the creation of an administrative body that would ensure waste disposal was practised in such a way as to minimize multi-media effects. This was reinforced in 1986 by the Cabinet Office Efficiency Unit, with the concern of haphazard pollutant disposal and inappropriate resource allocation when attempting to manage the environment through dealing separately with the three environmental media. A year later Her Majesty's Inspectorate of Pollution (HMIP) was established to administer environmental programs and develop industrial regulations.

In 1990, the UK produced an Environmental Protection Act which included Integrated Pollution Control (IPC) programs intended to integrate regulations through industry guidelines. The Act applies to all UK industry (currently the HMIP has developed regulations for the fuel and power, metal, chemical, mineral, and waste disposal industries), concentrating on the most potentially polluting or technologically complex industrial and other processes.

Substances and processes controlled under the Act were identified by the Secretary of State in The Environmental Protection (Prescribed Processes and Substances) Regulations 1991.

Processes are divided into two groups; Part A processes are subject to IPC and Part B processes are regulated by local authorities for air pollution control but subject to the special guidance of the Secretary. Part A processes are further broken down using three separate lists of prescribed substances which are referenced to the method or media of control (ie. control in air, water or land).

Prescribed processes are being phased in over a period of time (all industry to be regulated by 1995). After the phase in date, no prescribed process will be permitted to operate without authorization from HMIP. All applications for authorization must be advertised locally and HMIP must consider any related feedback. The legislation requires HMIP to maintain public registers which are to contain information regarding IPC applications, authorizations and monitoring information. The costs of administering the program are to be directly recovered through charging an application fee and annual charges based on the size and complexity of the process. The objectives of HMIP as set out in the Environmental Protection Act 1990 are:

- Best Available Technology Not Entailing Excessive Cost (BATNEEC) must be used to prevent or minimize prescribed substance release into environmental medium;
- releases must not breach direction of Secretary of State in meeting European Community or other international obligations; and
- when process likely to involve releases into more than one medium, that Best Practicable Environmental Option (BPEO) is achieved (ie. ensuring discharges are to the medium which results in the least environmental damage).

Direction to industry will primarily be provided through the use of guidance notes. Over 200 guidance notes will be produced for prescribed processes. HMIP's approach to preparing this information is to:

- review all BAT's of potential application to UK industry;
- produce draft agenda of key issues to be covered in the notes (ie. reasons for designating processes, existing process standards and standards HMIP believes achievable); and
- circulation of agenda to industry for comment followed by a revision process.

It is too early to observe the impact of the UK program as there has as yet been minimal feedback. One area of concern, expressed by the British Foundry Association (BFA), was the potential costs to industry of implementation of BATNEEC's, although this is more an issue of emission standards than the multi-media approach.

Hamburg, Germany - Integrated Pollution Control

The program established in Hamburg, Germany is an integrated permitting approach, integrated in terms of media and administrative jurisdictions. The program is supported by general provisions in German Federal environmental regulations, however, implementation is coordinated independently within each state. Consequently, different states can achieve notably different results. The IPC program in Hamburg is considerably more advanced than in other German states.

The Environment Protection division of the Environment Agency of the City of Hamburg contains the "Unit for Permits" which is responsible for permitting in the areas of air, noise, and water quality and waste. The organizational structure is such that responsibility for waste and air are integrated at the lowest level. The organization is segregated in terms of the type of source and facility rather than by medium so that permitting groups are applying media-specific laws and regulations to all regulated activities within a specific facility. The result is that cross-media effects are considered at all permitting levels.

The program of integrated permitting has been in effect since the early 1980's. The Federal legislation does not extend to the setting of emission standards, nor is the framework integrated at this level. The success of the program has been attributed to the existence of a very detailed Federal framework for environmental protection and the wide spectrum of responsibilities (in terms of types of activities and environmental media) within the agencies. The positive impact of the program is suggested by:

- the time required for application and permit processing has been reduced to approximately six months (present delays are attributed to involvement of local administrations);
- discussions on priority investment have been initiated with industry to establish

medium-term environmental strategies;

- officials are given a broad responsibility for entire facilities and therefore experience more efficient interactions with other government and industry parties; and
- the permitting procedure has resulted in a greater level of integrated environmental discussion throughout decision-making processes of applicants.

An industry contact noted that the integrated permitting approach has required more effort on the part of industry in dealing with the regulatory authorities, but that it has provided superior solutions to environmental problems.

Conclusion

There are sufficient examples of successful multi-media environmental management initiatives to lend strong support to the workability and success of this type of approach. Most of these programs are in early stages of development and will provide more information as their implementation proceeds. It is noteworthy that while not all programs are specifically aimed at pollution reduction, those involved in almost all the programs feel the multi-media approach will inevitably lead to reducing the total level of pollution.

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MUNICIPAL RECYCLING AND HOUSEHOLD CONSERVATION BEHAVIOUR A STUDY OF GUELPH, ONTARIO

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INTRODUCTION

Past environmental policies, particularly in waste management, have tended to favour a "hard" path, or reliance on physical technology, to solve environmental problems (Seldman, 1980). Bureaucrats have tended not to trust people-oriented technology. The social dimension in environmental policy implementation has largely been ignored, even where it is most obvious -- in the implementation of policies and programs aiming to influence the separate decisions of millions of individuals (Stern and Oskamp, 1987).

Increasingly, however, environmental problems are being recognized as essentially human behavioural problems of lifestyle and habits, of ignorance, and of motivation (Cone and Hayes, 1980). Promotion of environmentally-responsible behaviour of individuals is now accepted as as a crucial element in public policy addressing these problems. The success of current conservation programs, for example, Ontario's municipal curbside waste recycling program, also known as the "Blue Box" program, is encouraging and may prove educational not only for participants but for policy-makers hoping to build on their success.

There are many elements to the success of conservation programs: economic viability; environmental improvement; and the ability of the program to change human behaviour. This paper addresses the latter, specifically, the nature and extent of individual participation in municipal recycling programs, and the effect of participation in these programs on the adoption of other forms of environmentally-responsible behaviour. In contrast to an extensive literature on environmental attitudes, very few studies describe the nature and extent of environmentally-responsible behaviour (Tracy and Oskamp, 1983-84; Stern and Oskamp, 1987). Even less evident in the literature is any attempt to relate the adoption of one form of conservation behaviour to the adoption of others, as a learning cycle.

It is hypothesized that participation in municipal recycling programs affords a form of social learning, allowing individuals to derive knowledge and skill in conservation activities which may predispose them to adopt other forms of conservation behaviour. The more rigorous the involvement in waste separation activities, the more likely individuals are to acquire personal experience and knowledge about waste reduction and recycling, which may lead them to develop positive feelings about environmentally-responsible behaviour. These positive attitudes, particularly toward the activity itself, may create or reinforce environmental attitudes, influencing the adoption of other forms of environmentally-positive behaviour (De Young, 1986).

The objectives of this paper are, in the context of a sample of City of Guelph households, to:

1. describe the nature and extent of recycling behaviour and selected forms of other environmentally-responsible behaviour (energy conservation, water conservation and consumer behaviour); and,

2. determine the relationship between the degree of involvement in municipal recycling programs and: 1) energy conservation; 2) water conservation; and 3) consumer behaviour.

METHODOLOGY

Study Area

The City of Guelph's pioneering efforts in waste management afford an unique opportunity to study the influence of several levels of recycling activity. The Blue Box program, operational for about four years, collects newspapers and glass, tin and plastic containers, and diverts about 18% of waste from landfill. The innovative Wet Dry program, operational on a limited test basis for almost two years, requires individuals to undertake a more sophisticated form of source separation of waste in the home. Wet, compostable, materials such as food waste and grass clippings are placed in a green bin; dry, recyclable and non-recyclable, materials (except hazardous waste) are placed in a blue bin. Several variations of the Wet Dry program are being tested, but all divert at least 62% of waste (City of Guelph, 1991).

Sample Frame and Respondent Selection

The research approach adopted was to elicit information from participants in Guelph's Blue Box and Wet Dry recycling programs through an interview-administered questionnaire. The study was confined to households in single family dwellings in order to maintain as much consistency as possible in opportunities for involvement in household conservation behaviour.

Blue Box participants in four selected neighbourhoods were randomly sampled. Neighbourhoods were chosen to reflect a range of socio-economic conditions. The Wet Dry program has been available in only one area of the city; households in this pilot area were also randomly sampled.

Sampled households were visited on as many as three occasions to establish contact with an adult respondent, before a substitution was made. In most cases, an adjacent residence served as the substitute. Only several contacted individuals declined to be involved in the study; ultimately, respondents in 161 households were interviewed. 80 were participants in the Blue Box program and 81 were participants in the Wet Dry program.

Data Collection and Analysis

Two questionnaires, differing slightly due to the nature of the recycling programs involved, were designed to obtain data necessary to satisfy the study objectives. The questionnaire sought information on the nature and extent of household participation in municipal recycling and selected forms of other household conservation behaviour (energy conservation, water conservation, consumer behaviour). A key feature was the effort to identify how households disposed of 17 waste items, including several such as aerosol cans and magazines thought to pose problems for some households in determining appropriate disposal. Respondents were also questioned on the frequency of selected conservation behaviour and the length of time such behaviour had been practiced (to facilitate comparison of pre- and post-recycling conservation behaviour). To facilitate controlling other factors potentially influencing household conservation behaviour, while exploring the relationship between recylcing and other behaviour, data were sought on selected characteristics of households, for example, household size and age and education of respondents.

To provide an aggregate description of household recycling and other conservation activities, and to facilitate analysis of the relationship between these behaviours, indexes were constructed for each form of conservation behaviour. For energy and water conservation and consumer behaviour, responses to questions on specific behaviour were scored and weighted to recognize variations in commitment of time and capital to particular conservation activities and devices. The weighted scores ranged from zero to 18, 14, and 20, respectively, for energy conservation, water conservation, and consumer behaviour.

Indexes for Blue Box and two variations of Wet Dry recycling were constructed from responses detailing how households disposed of selected waste items. Points were awarded for appropriate disposal, for example, vegetable peelings to the green bin (Wet Dry participants) or a backyard composter (Blue Box participants). Points were also deduced for inappropriate disposal, for example, paint cans in the blue bin or Blue Box. The theoretical range of recycling scores was -16 to 68 and -23 to 68, respectively, for Blue Box and Wet Dry participants.

Differences among Blue Box and Wet Dry respondent groups, in terms of household characteristics and conservation behaviour, were evaluated by t-test and chi-square analysis.

FINDINGS

Social Characteristics of Study Respondents

A major objective of the study was to explore the influence of recycling behaviour, specifically participation in two recycling programs, on other household conservation behaviour. Thus, it was important to examine the social characteristics of recyclers, as these may influence conservation behaviour. Blue Box and Wet Dry respondents were examined in terms of age, education, lifestyle, size of household, number of children and pre-school children in household, and length of residence in Guelph. Lifestyle attempted to capture the amount of time available to devote to recycling and other conservation activities in the home. For instance, households with both adults working outside the home were distinguished from retired persons.

No statistically significant differences between Blue Box and Wet Dry respondents were found in any of the above attributes, with the exception of education. A significantly higher proportion of Wet Dry (20.3%) compared to Blue Box (7.5%) respondents were university graduates. This reflects the City's choice of a pilot study area for the Wet Dry program, a neighbourhood near the University of Guelph in which a number of active and retired university faculty and staff reside. As education is potentially a powerful influence on behaviour, this difference between Blue Box and Wet Dry respondents is important, and will have to be reflected in any analysis undertaken to explore the influence of recycling behaviour on other conservation behaviour.

Household Conservation Behaviour

Recycling Behaviour

Theoretically, recycling scores can range from -16 to 68 for Blue Box participants, and from -23 to 68 for Wet Dry participants. The mean score of 50 for Wet Dry respondents was almost twice the mean score of 27 for Blue Box respondents. The range of scores for both recycling groups was similar. In intrepreting this marked difference in recycling scores, it should be noted that Blue Box recycling involves curbside collection of only a limited number of waste items (newspapers and metal, glass, and rigid plastic containers). To obtain a high score, a Blue Box participant would have to make some use of recycling facilities elsewhere, notably Guelph's central recycling depot.

A generally high degree of commitment among Wet Dry participants in sorting waste items is evident. Some of the waste items selected for study, however, posed problems for a number of respondents. Over a third of respondents incorrectly disposed of light bulbs, aerosol cans and styrofoam; a smaller proportion appropriately disposed of paint cans.

While a few Blue Box respondents had very high recycling scores, the level of commitment to recycling was generally lower. Over half of respondents inappropriately disposed of aerosol cans, corrugated cardboard, and egg cartons; fine paper and magazines were also problem items for many respondents. As well, a proportion of Blue Box recyclables are lost to the garbage stream. Some 31 percent of Blue Box respondents reported sometimes, often, or always discarding rigid plastic containers into the garbage; 19, 17, and 6 percent of respondents indicated they at least sometimes discarded metal cans, glass containers, and newspapers, respectively.

A good indicator of the comparative commitment of Blue Box and Wet Dry respondents to waste management is their handling of household hazardous waste items. Proper treatment of these waste items requires participants of both the Blue Box and Wet Dry programs to take these items to the city's central hazardous waste depot. It is notable that in all cases a higher proportion of Wet Dry respondents made the effort to do so.

Other Conservation Behaviour

Other household conservation behaviour measured were energy and water conservation and consumer behaviour. Examples of energy conservation are use of a clothes line, energy efficient light bulbs, and a night set-back thermostat. Water conservation was measured by such actions as turning water on and off to brush teeth, and installation of toilet dams. Examples of consumer behaviour are use of reusable shopping bags, purchase of drinks in returnable bottles, and membership in environmental organizations.

For all respondents, conservation scores were moderate for energy conservation (mean score of 8 out 18), lowest for consumer behaviour (mean score less than 5 out of 20). The mean water conservation score was 5 (out of 14). This distribution of mean scores is not unexpected. Energy conservation has been an issue since the mid 1970s, and many forms of energy conservation offer direct cost savings to households. Water conservation is gaining some momentum in southern Ontario (Kreutzwiser and Feagan, 1989), but is not yet a local issue, no doubt due in part to Guelph's very adequate water supplies. Concern for the environmental implications of consumer products is largely a very recent phenomenon and not yet well developed.

Recylcing and Other Household Conservation Behaviour

A primary objective of this study was to explore the relationship between participation in municipal recycling programs and other forms of household conservation behaviour. Analysis revealed that only for consumer behaviour is there a significant difference in mean conservation scores between participants in the Blue Box and Wet Dry programs. The mean consumer behaviour score for Wet Dry respondents was over 30 percent higher than the score for Blue Box respondents. The implication is that participation in the more demanding Wet Dry program has encouraged many respondents to rethink their purchasing practices.

The influence of participation in the Wet Dry recycling program on consumer behaviour, however, is clouded by the statistically significant difference in the educational characteristics of the Blue Box and Wet Dry study groups. To address this concern, further analysis was undertaken. Table 1, for example, compares the recycling and other conservation scores of Blue Box and Wet Dry respondents, exclusive of those in the highest educational category (those with at least one university degree). While the consumer behaviour score is no longer significantly different, the mean score for Wet Dry respondents remains substantially higher than for Blue Box respondents.

TABLE 1

CONSERVATION SCORES FOR WET DRY AND BLUE BOX GROUPS EXCLUDING THE HIGHEST EDUCATIONAL CATEGORY

		Mean Score	SD	Range	T Value
Recycling Score (/68)	BB =	27.20	12.92	-10-64	0.0000*
	WD =	47.66	17.00	-6-68	
Energy Conservation Score (/18)	BB =	8.16	3.67	0-16.0	0.3776
	WD =	7.62	3.42	0-17.5	
Water Conservation Score (/14)	BB =	5.09	2.96	0-12.0	0.3393
	WD =	4.59	3.11	0-12.0	
Consumer Behaviour Score (/20)	BB =	3.99	3.58	0-17.0	0.2032
	WD =	4.79	3.78	0-16.0	

Blue Box Group = BB (N=79)
Wet Dry Group = WD (N=62)

* significant at 95% confidence level

Differences in mean conservation scores between the two recycling groups were also analyzed separately for both the higher and lower educational categories. Importantly, Wet Dry respondents in each category had higher consumer behaviour scores. The difference was statistically significant only for the higher education group.

In assessing the influence of participation in municipal recycling programs on other forms of household conservation behaviour, an important feature of these programs should be kept in mind. Guelph households can access information on recycling and municipal solid waste management from a variety of sources, including family, friends, television, newspapers, and newsletters and brochures prepared and distributed by the municipality. As part of the pilot Wet Dry program, a substantial effort was expended to inform households about the program and the waste management issue more generally (Gibson, 1991). Two public meetings were held prior to program start-up, and a third meeting at the end of the program's first year. Information was supplied when the green and blue bins were distributed, and several program update letters were subsequently sent to participants. Participants were also asked to contact city staff about program implementation, and many have done so. Largely as a consequent of this effort to inform, a significantly higher proportion of Wet Dry respondents (27 percent compared to 14 percent of Blue Box respondents) reported municipal brochures and newletters as the most frequently used source of information on the waste issue.

CONCLUSIONS

Blue Box municipal recycling programs have been widely acknowledged as successful. These programs continue to effect a modest but important reduction in solid waste requiring landfilling or incineration. They conserve increasingly scarce material and energy resources. More aggressive recycling programs, such as the Wet Dry program proposed for full implementation in the City of Guelph, will enhance these benefits.

This paper, however, has been concerned with a rather different potential benefit of municipal recycling. It was hypothesized that participation in municipal recycling programs represents a form of social learning, predisposing individuals to adopt other forms of conservation behaviour and to express environmentally positive attitudes. Differences in selected household conservation behaviours, between participants in the basic Blue Box program and more involved Wet Dry program, were expected.

Evidence derived from this study, however, offers only limited confirmation of this benefit. No differences in waste management attitudes or in household energy and water conservation behaviour, between participants in Guelph's Blue Box and Wet Dry recycling programs, were observed. Environmentally-responsible consumer behaviour, as measured by such actions as using a reusable shopping bag, purchasing drinks in returnable bottles, and refusing to purchase over-packaged products, was significantly greater among Wet Dry participants. This difference was also evident after the influence of respondents' educational level was eliminated, though it was not statistically significant.

The apparent influence of participation in municipal recycling on conservation-minded consumer behaviour can be understood in terms of the nature of these forms of behaviour. No doubt, participation in the more demanding Wet Dry program has heightened awareness of the waste implications of various consumer products and practices. The more extensive information process connected with the pilot Wet Dry program also likely influenced consumer behaviour. This information effort involved personal contacts between city staff and many participants.

The findings of this study offer several practical suggestions for the design and implementation of municipal recycling and other conservation programs. While a much higher level of recycling was achieved by participants in the pilot Wet Dry program, compared to the conventional Blue Box program, some waste items were found to be particularly troublesome. For both groups, hazardous waste items such as aerosol cans and paint cans are notable. However, a much higher proportion of Wet Dry participants properly disposed of these and other hazardous items at Guelph's Hazardous Household Waste Depot. Moreover, within the Wet Dry group, participants in the two stream version (without a garbage option) were particularly diligent using this Depot.

It is also notable that after four years of experience with the Blue Box program, a substantial proportion of participants are incorrectly placing magazines and fine paper in the Blue Box. Some of these individuals may be misinformed, others may simply be careless. This does raise, however, the issue of the role of information in municipal recycling and other conservation programs.

It was earlier noted that a distinguishing feature of Guelph's pilot Wet Dry program was the considerable effort made to inform participants about the purpose and functioning of this program. No doubt as a consequence, almost twice the proportion of Wet Dry (compared to Blue Box) respondents reported city brochures as their most frequently used source of information on municipal solid waste. While this observation is not offered as justification for an intensive information component to any recycling or conservation program, it does suggest that the design and delivery of program information is important.

Finally, the findings of this study, regarding the relationship between participation in municipal recycling programs and other forms of household conservation behaviour, raise the possibility that only closely related conservation behaviour may be influenced by participation in municipal recycling programs. This issue needs to be explored more thoroughly. A broader relationship may exist, for example, to which data collection and analysis were insensitive. If, however, only closely related behaviour may be positively influenced, this should be recognized in the design of public programs aiming to encourage environmentally-responsible behaviour.

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PSYCHOSOCIAL EFFECTS IN POPULATIONS EXPOSED TO SOLID WASTE FACILITIES

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INTRODUCTION

This paper describes the results of logistic regression analyses performed on epidemiologic survey data collected from populations living in close proximity to three solid waste facilities in southern Ontario. Psychosocial effects are defined as the complex of distress, dysfunction and disability manifested in a wide range of psychological, social and behavioural outcomes as a consequence of actual or perceived environmental contamination.

The most useful theoretical framework for informing this research comes from the environmental stress and coping literature [1,2,3]. Baum et al. [4, p. 186] define environmental stress as "a process by which environmental events threaten, harm or challenge an organism's existence or well-being and by which the organism responds to this threat." A useful psychological model of response to environmental stress is that provided by Lazarus and Folkman [3]. This model contends that response to environmental stress is divided into two basic stages: ***primary*** appraisal whereby the individual appraises an environmental stressor as a threat, a harm, or a challenge; ***secondary*** appraisal whereby one of two basic coping strategies is selected: (1) problem-focused coping (e.g., joining a citizen's action group), or (2) emotion-focused coping (e.g., adjusting attitudes towards the stressor). ***Reappraisal*** occurs as the perception of the stressor or available coping resources changes over time.

The experience of environmental stress, the choice of a particular coping response and the incidence of psychosocial effects are dependent upon a number of mediating factors which can be categorized into four sets: characteristics of the environmental stressor [5,6,7]; characteristics of the individual [6,8]; characteristics of the social network [9,10]; and characteristics of the wider community system [7,9,11]. This categorization defines the structure of the conceptual framework for the current study (Figure 1).

STUDY DESIGN

The objectives of the study are:

1. *To determine the prevalence of psychosocial effects among exposed individuals.*

2. *To investigate the determinants of individual level psychosocial effects.*

3. *To investigate the determinants of individual level actions taken in response to psychosocial effects.*

A set of evaluation criteria [12] led to the selection of three solid waste disposal facilities in southern Ontario: the Solid Waste Reduction Unit (SWARU) in Hamilton, the Hamilton-Wentworth Regional landfill site in Glanbrook and the recently approved Halton Regional Landfill in the Town of Milton (Figure 2). The project follows a parallel case-study design in which each site comprises an independent study. The primary analyses reported in this paper are therefore by site.

The epidemiologic survey was administered by phone to a disproportionate stratified random sample of 250 households across four zones around each of the three sites. This stratification procedure allows for the use of internal controls, based on distance from the site, in subsequent analyses. Zone distances were not uniform across sites as both Glanbrook and Milton are rural areas with characteristically low population densities (Table 1).

TABLE 1: SAMPLE DESIGN

SITE	ZONE 1 km	ZONE 2 km	ZONE 3 km	ZONE 4 km	TOTAL DISTANCE (km)
SWARU	1	.5	.5	.5	2.5
GLANBROOK	2	1	1	1	5
MILTON	2	1	1	.5	4.5

The instrument was introduced as a general quality of life survey. Essentially, it consists of five sections: (1) attitudes toward the neighbourhood or home area including factors liked and disliked and ratings of satisfaction; (2) social networks reflecting their possible mediating influence on psychosocial effects; (3) measures of psychosocial health and well-being (the 20 item version of the General Health Questionnaire (GHQ-20) [13] and the somatic symptom checklist from the Symptom Check List-90 (SCL-90) [14] as well as a subset of items from the Critical Life Events Scale [15]); (4) a combination of closed- and open-ended items to determine residents' levels of awareness, knowledge, concern and action regarding the site or more general environmental problems, with particular emphasis on health concerns; and, (5) standard socio-demographic variables as a check on the characteristics of the sample and its representativeness and as potential mediators of psychosocial effects for inclusion in the analysis.

Eligible respondents were adult members of the household selected via a random selection procedure to ensure gender representativeness. Between May and July 1990, 696 interviews were completed across the three sites (Table 2).

TABLE 2: SAMPLE SIZE

SITE	ZONE 1	ZONE 2	ZONE 3	ZONE 4	SITE TOTAL
SWARU	77	55	58	64	[illegible]
GLANBROOK	52	67	71	65	[illegible]
MILTON	44	38	58	47	[illegible]

ANALYTICAL MODEL AND METHOD

The analytical model which guided the analysis of the survey data has three main components: external variables (e.g., individual and exposure-related variables); mediating variables (e.g., social network membership and involvement, general health status measures); and outcome variables (e.g., concern, effects and coping responses) (Figure 3). Logistic regression models were run using backward-stepwise regression for outcomes *concern*, *health concern* and *actions*. Due to their *a priori* importance, the variables age, gender and zone were forced into every model regardless of their contribution. Once all important explanatory variables were identified through the modelling process, first-order interaction terms were entered using forward-stepwise regression. These interaction terms took two forms: (1) age, gender and zone by each remaining independent variable, and (2) each remaining independent variable with all others.

RESULTS

Concern

Concern was measured by asking respondents whether or not they had any concerns about the site in their area. Frequencies indicate that the overall level of concern reported at SWARU is low (28%) relative to the other two sites (Milton 74%, Glanbrook 67%). There is some evidence at each site of a gradient of concern. This is clearest at Milton with 91% of respondents in the closest zone reporting concern, 82% in zone 2, 67% in zone 3 and 62% in zone 4. The specific concerns most frequently mentioned were: air pollution (SWARU), site operation (Glanbrook) and water pollution (Milton).

The logistic regression model of *concern* at SWARU (Table 3) has a rho^2 of .23. The model has good specificity (an indicator of false negative predictions) at 81% but lower sensitivity (an indicator of false positive predictions) at 68%. Overall, 79% of cases were correctly classified. Based on the significant single effects in the model (the shaded cells in Table 3), a respondent at SWARU more likely to be concerned is: satisfied with current health status, has been worried about someone over the past 12 months, belongs to a labour union or commercial group and has a score on the GHQ-20 above the cut-point for normal [13]. In addition, the significant interaction effects indicate that the person more likely to be concerned owns a dwelling and belongs to a labour union or commercial group, had a spouse or partner die in the past 12 months and has a GHQ-20 score above normal, owns a dwelling and lives closer to the site (as opposed to renting and living closer to the site).

The model of *concern* at Glanbrook has a rho^2 of .22. The model has good sensitivity (79%) but lower specificity (69%). Overall, 76% of cases were correctly classified. Based on the significant single effects in the model (shaded cells in Table 3), a respondent at Glanbrook more likely to be concerned: lives in zone 1 as opposed to zone 4, has lived longer at current address, has more close friends, is not satisfied with social activities, participates in fewer helping behaviours with neighbours than previously, and, belongs to an environmental group. In addition, the significant interaction effects indicate that the person more likely to be concerned: is not satisfied with social activities and has lived fewer years at their current address, is younger and has fewer years at current address, and, female and not satisfied with the area.

The model of *concern* at Milton has a rho^2 of .40. Both sensitivity (91%) and specificity (78%) are high. Overall, 88% of cases were correctly classified. Based on the significant single effects in the model (shaded cells in Table 1) a respondent at Milton more likely to be concerned lives in zone 1 as opposed to zone 4, has been worried about someone over the past 12 months, has a score on the SCL-90 somatic symptom checklist above the normal cut-point [14], and, has had greater past community involvement. In addition, the significant interaction effects indicate that the person more likely to be concerned is not satisfied with social activities and has not been worried about anyone over the past 12 months, is younger and has had less past community involvement.

Several points can be made from these analyses. First, the heterogeneity of the models must be acknowledged. This points to the differences in site and population characteristics and their influence on psychosocial effects of exposure (Figure 1). Second, these results illustrate that in this case there is no simple cause and effect relationship between exposure and concern. While distance from the site was a significant explanatory variable at two of the sites, numerous other variables from various blocks of the analytical model also contribute to the models. Third, the analysis of the Milton site confirms the suggestion that psychosocial effects occur whether exposure is actual *or perceived*. Finally, it would appear that social network factors are more strongly related to concern in the rural study areas (Glanbrook and Milton) than in the urban area (SWARU).

Health Concern

Respondents were asked whether they considered their concerns to be health related. Again, the lowest level of health concern reported was at SWARU with 21%, the highest at Milton with 52%, and Glanbrook in the middle with 49%.

The logistic regression model of *health concern* at SWARU (Table 4) has a rho^2 of .22. Specificity is high (85%) but sensitivity is low (60%), perhaps a result of the low levels of reported health-related concern at this site. Overall, 83% of cases were correctly classified. The significant explanatory variables which comprise this model (the shaded cells in Table 4) indicate that a respondent at SWARU whose concerns are health related belongs to an environmental group and is more likely to have a household income in the $60-$70,000 range. The one significant interaction term suggests that higher levels of health-related concerns are found in individuals who ask for or receive help from neighbours very often and have a score on the SCL-90 somatic symptom checklist above the normal cut-point.

The model of *health concern* at Glanbrook has a rho^2 of .22. Sensitivity (80%) and specificity (77%) are both high. Overall, 77% of cases were correctly classified. Based on the significant single effects in the model (shaded cells in Table 4) a respondent at Glanbrook whose concerns are more likely to be health related is: older (although, age has a borderline t-value), lives in zone 2 as opposed to zone 4, has an SCL-90 score above the cut-point, and, belongs to an environmental group. In addition, the significant interaction effects indicate that the person more likely to have health concerns is female and has not had a recent serious illness, is female and belongs to a community group not named by the respondent, lives in zone 1 or 2 and has a score on the SCL-90 below the cut-point.

The model of *health concern* at Milton has a rho^2 of .22. Both sensitivity (76%) and specificity (75%) are high. However, the only significant variable in the model (Table 4) is 'past community involvement'. This is a summary measure of the number of activities respondents may have taken part in regarding a local community issue. Its significance in this model has two potential interpretations; (1) respondents in Milton are very active regarding community issues; or, (2) due to the recency of the Milton siting, the local community issue respondents were involved in was the study site and they are therefore very aware of potential health implications of a landfill.

Again, the models for *health concern* are very different for the three sites indicating the uniqueness of each of the case studies and the points made earlier for the models of concern apply equally here. On the other hand, a common feature of the three models is the consistent significant effect of variables related to involvement in community and environmental issues.

Actions

Respondents were asked if they had participated in one or more of a variety of site-related actions. The lowest frequency is again at SWARU (21%), the highest is at Milton (71%), and Glanbrook is in the middle (60%). In addition, there is clear evidence of a gradient of actions away from each of the three sites, with the highest levels of reporting in the zones closest to the sites.

The model of *actions (1+)* at SWARU (Table 5) has a rho^2 of only .19. Specificity is 82% but sensitivity is only 63%, again likely related to the low frequency of actions taken at this site. Overall, 80% of cases are correctly classified. A respondent at SWARU more likely to take one or more actions in response to site concerns (shaded cells in Table 5): lives in zone 1 as opposed to zone 4, owns a dwelling, is not satisfied with the area in which they live, does not belong to a children's group but does belong to more community groups than someone less likely to take action.

The model of *actions (1+)* at Glanbrook has a rho^2 of .23. Specificity is relatively low (69%) but sensitivity is high (94%). Overall, 73% of cases were correctly classified. Based on the single significant effects in the model (shaded cells in Table 5) a respondent at Glanbrook more likely to take at least one action in response to site-related concerns: lives in zone 1, has fewer close relatives and more close friends, perceives him/herself as being somewhat involved in their community as opposed to not at all involved, and, is a member of an environmental group. In addition, the significant interaction effects indicate that a respondent more likely to take action has had less past community involvement and does not perceive him/herself to be very involved in the community currently. This last interaction term perhaps implies that individuals who are not active in the community may become sufficiently aroused by a landfill siting to take action.

The model of *actions 1+* at Milton has a rho^2 of .23. Sensitivity is high (81%) but specificity is low (56%). Overall, 74% of cases were correctly classified. The significant explanatory variables which comprise this model (the shaded cells in Table 5) are few. A respondent at Milton who is more likely to take at least one action is also more likely to live in zone 1 as opposed to zone 4, talk with neighbours very often as opposed to never, and belong to a community group not named by the respondent.

These action-related models are dominated by social network variables which indicate an individual's connectedness to both primary and secondary social networks as well as the wider community system of which these are a part. This again supports the use of a socioecological approach when investigating psychosocial effects of exposure (Figure 1).

DISCUSSION

Zone emerged as an important explanatory variable in several of the models. This points to the importance distance from the site plays in the process of psychosocial effects and confirms the distance gradients apparent in the outcome variable frequencies. However, given the number and mix of explanatory variables in all the models, a simple cause and effect relationship is not supported.

The results indicate that social network variables had significant single effects in all the models. While significant variables from all blocks enter the concern-related models, social network variables clearly dominate the action models. It appears that those respondents connected to the community in other ways are also those taking action.

Variables related to general health status were included as potential mediators of site-specific effects. Items from the Holmes and Rahe stressful life events scale [15] were significant in two of the models (concern at SWARU and Milton). The GHQ-20 and SCL-90 measures of emotional distress were significant in 4 of the models: higher levels of emotional distress were related to concern (SWARU and Milton), health concern (Glanbrook) and action (Milton). Perceived health status was significant in only one model: concern at SWARU. A fundamental difficulty in interpreting these results is the uncertain cause and effect linkages. The variables age and gender were deemed to be of *a priori* importance given their significance in the environmental stress literature. However, as a single term, age achieved (borderline) statistical significance only once (health concern at Glanbrook). Gender also proved to be of little importance despite the findings of other studies (e.g., Three Mile Island) which indicate higher levels of psychosocial effects among women. Related to this, the presence of young children in the home did not emerge as a significant explanatory variable.

Individual level variables rarely emerged as significant explanatory variables with the exception of length of residence (both 'in the area' and 'at current address'). Dwelling tenure and type often emerge as important variables in understanding concern around other noxious facilities [16]. There was little variation in these variables at two sites which could perhaps explain their absence from the models. The same argument could account for the lack of effect of socioeconomic status (measured as income, education and occupational status).

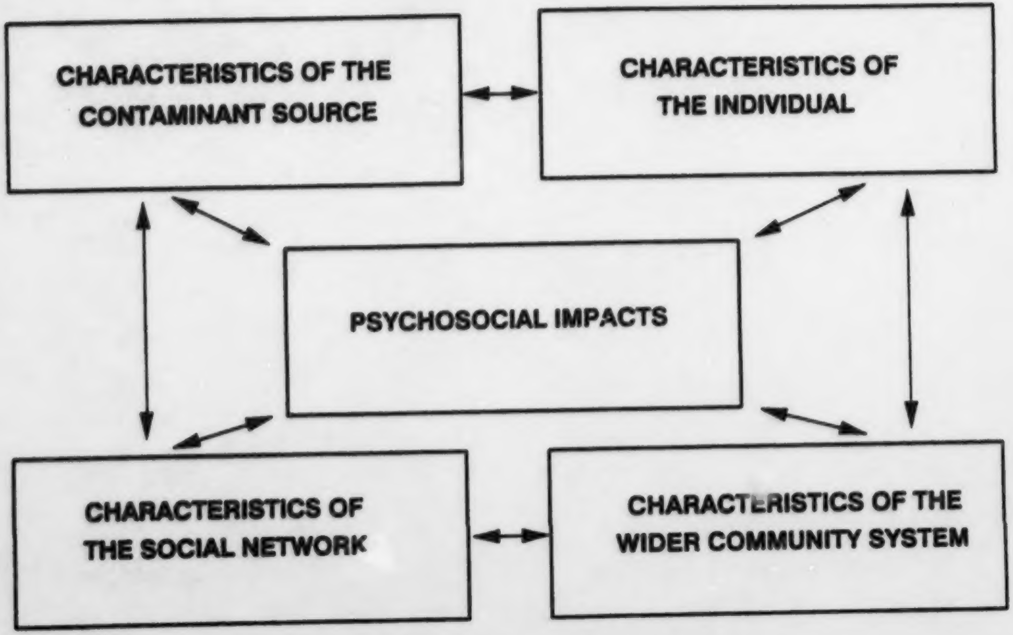
CHARACTERISTICS OF THE CONTAMINANT SOURCE
CHARACTERISTICS OF THE INDIVIDUAL
PSYCHOSOCIAL IMPACTS
CHARACTERISTICS OF THE SOCIAL NETWORK
CHARACTERISTICS OF THE WIDER COMMUNITY SYSTEM

FIGURE 1: CONCEPTUAL FRAMEWORK

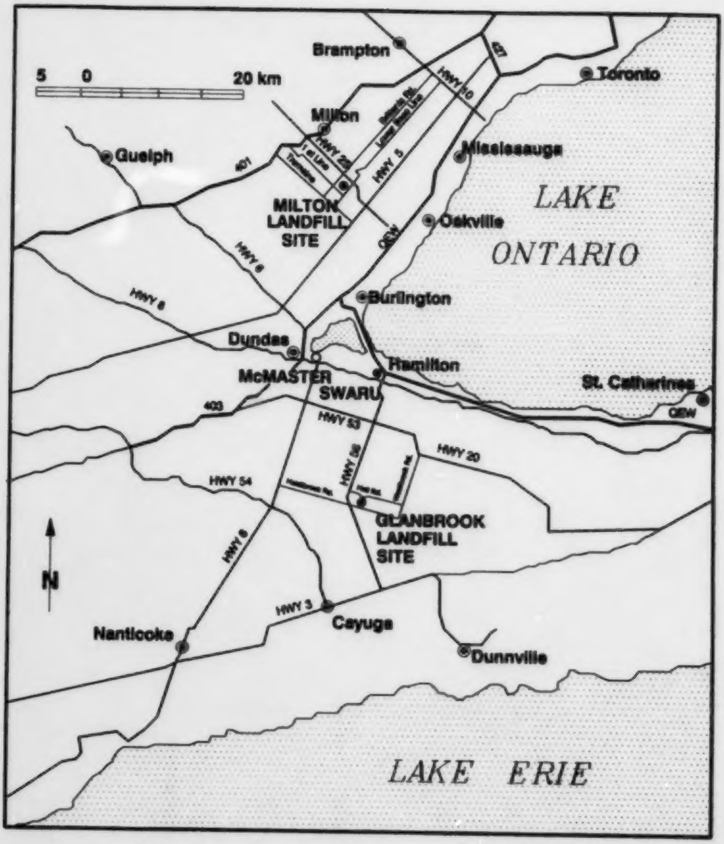
Brampton
5 0 20 km
Toronto
HWY 10
407
Milton
HWY 25
HWY 5
Mississauga
Guelph
401
1st Line
MILTON LANDFILL SITE
LAKE ONTARIO
Oakville
QEW
HWY 6
HWY 8
Burlington
Dundas
Hamilton
McMASTER
SWARU
St. Catharines
QEW
403
HWY 53
HWY 20
HWY 54
HWY 56
GLANBROOK LANDFILL SITE
N
HWY 6
HWY 3
Cayuga
Nanticoke
Dunnville
LAKE ERIE

FIGURE 2: STUDY SITES

FIGURE 3:
ANALYTICAL MODEL: EPIDEMIOLOGIC SURVEY

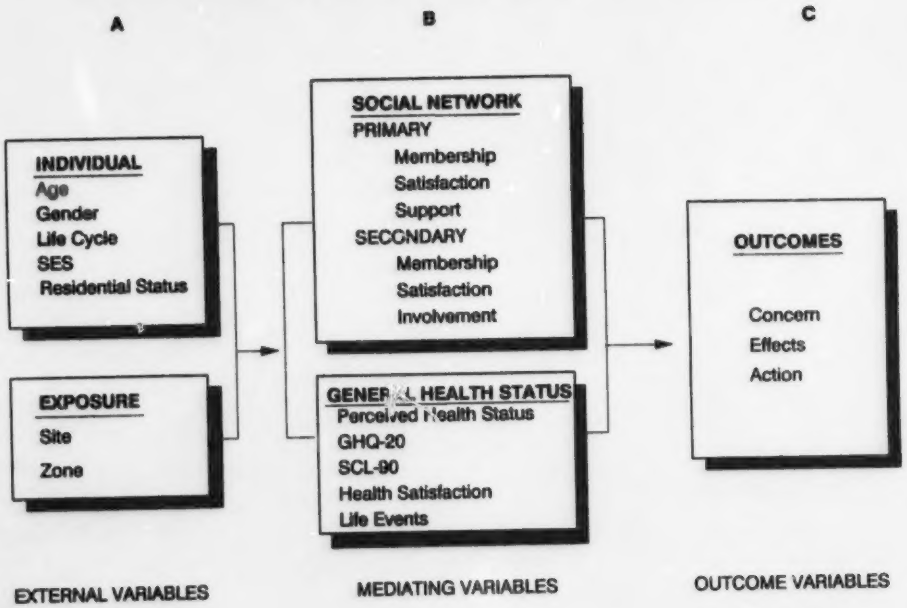
A
B
C
INDIVIDUAL
Age
Gender
Life Cycle
SES
Residential Status
EXPOSURE
Site
Zone
SOCIAL NETWORK
PRIMARY
Membership
Satisfaction
Support
SECONDARY
Membership
Satisfaction
Involvement
GENERAL HEALTH STATUS
Perceived Health Status
GHQ-20
SCL-90
Health Satisfaction
Life Events
OUTCOMES
Concern
Effects
Action
EXTERNAL VARIABLES
MEDIATING VARIABLES
OUTCOME VARIABLES

TABLE 3: EXPLANATORY VARIABLES FOR OUTCOME: CONCERN

SWAREU	GLANBROOK	MILTON
AGE	AGE	AGE
GENDER	GENDER	GENDER
ZONE ZONE 1 ZONE 2 ZONE 3	ZONE ZONE 1 ZONE 2 ZONE 3	ZONE ZONE 1 * ZONE 2 ZONE 3
HEALTH SATISFACTION ***	# CLOSE FRIENDS *	PAST COMMUNITY INVOLVEMENT **
WORRIED ABOUT ANYONE *	SATISFACTION WITH SOCIAL ACTIVITIES **	WORRIED ABOUT ANYONE **
ASK FOR OR RECEIVE HELP FROM NEIGHBOURS NEVER SELDOM SOMETIMES OFTEN	FREQUENCY HELP/ BEING HELPED BY NEIGHBOURS MORE FREQUENTLY ABOUT THE SAME **	EDUCATION < HIGH SCHOOL COMP. HIGH SOME COLL. COMP. COLL. SOME UNIV. +
BELONG LABOUR UNION/COMMERCIAL GRP **	# YEARS AT CURRENT ADDRESS ***	CONFIDANT *
GHQ-20 SCORE *	BELONG ENVIRON. GRP **	SCL-90 SCORE *
DWELLING TENURE	SOCIAL SATISFACTION X # YEARS **	# YEARS IN RESIDENCE X EDUCATION < HIGH SCHOOL COMP. HIGH SOME COLL. COMP. COLL. SOME UNIV. +
DWELLING TENURE X GRP *	AGE X # YEARS **	SOCIAL SATISFACTION X WORRIED ABOUT ANYONE
AGE X WORRIED	GENDER X AREA SATISFACTION *	AGE X PAST COMMUNITY INVOLVEMENT
SPOUSE/PARTNER DIE X GHQ-20 SCORE *	ZONE X # YEARS IN AREA ZONE 1 ZONE 2 ZONE 3	
ZONE X DWELLING TENURE ZONE 1 X RENT ZONE 2 X RENT ZONE 3 X RENT *		
% CORRECT 79%	% CORRECT 76%	% CORRECT 80%
SPECIFICITY 81%	SPECIFICITY 69%	SPECIFICITY 70%
SENSITIVITY 68%	SENSITIVITY 79%	SENSITIVITY 91%
rho^2 .23	rho^2 .22	rho^2 .40

*** $p < .001$ ** $p < .01$ * $p < .05$

TABLE 4: EXPLANATORY VARIABLES FOR OUTCOME: HEALTH CONCERN		
SWARU	GLANBROOK	MILTON
AGE	AGE *	AGE
GENDER	GENDER	GENDER
ZONE ZONE 1 ZONE 2 ZONE 3	ZONE ZONE 1 * ZONE 2 ZONE 3	ZONE ZONE 1 ZONE 2 ZONE 3
BELONG LABOUR UNION/COMMERCIAL GRP	'OTHER' GROUP	PAST COMMUNITY INVOLVEMENT **
BELONG ENVIRONMENTAL GRP *	ENVIRONMENTAL GROUP ***	GENDER X DWELLING TENURE
INCOME [illegible] [illegible] [illegible] [illegible] [illegible] * [illegible] [illegible]	CHILDREN < 5 YEARS	ZONE X EDUCATION
HEALTH SATISFACTION	# YRS CURRENT ADDRESS	
SCL-90 SCORE	RECENT SERIOUS ILLNESS	
REC. SUPPORTIVE HELP FROM NEIGHBOURS X SCL-90 SCORE NEVER X BELOW SELDOM X BELOW SOMETIMES X BELOW ** OFTEN X BELOW	SCL-90 SCORE ***	
	AGE X CHILDREN < 5 YRS	
	GENDER X RECENT SERIOUS ILLNESS **	
	GENDER X OTHER GRP **	
	# YRS CURRENT ADDRESS X 'OTHER' GRP	
	ZONE X SCL-90 SCORE 1 X BELOW ** 2 X BELOW ** 3 X BELOW	
% CORRECT 83%	% CORRECT 77%	% CORRECT 76%
SPECIFICITY 85%	SPECIFICITY 77%	SPECIFICITY 75%
SENSITIVITY 60%	SENSITIVITY 80%	SENSITIVITY 76%
rho^2 .22	rho^2 .22	rho^2 .22

*** $p < .001$ ** $p < .01$ * $p < .05$

TABLE 5: EXPLANATORY VARIABLES FOR OUTCOME: ACTIONS

SWARU	GLANBROOK	MILTON
AGE	AGE	AGE
GENDER	GENDER	GENDER
ZONE ZONE 1 * ZONE 2 ZONE 3	ZONE ZONE 1 *** ZONE 2 *** ZONE 3 *	ZONE ZONE 1 *** ZONE 2 ZONE 3
CONFIDANT	# CLOSE RELATIVES **	FREQUENCY TALK WITH NEIGHBOURS NEVER ** SELDOM SOMETIMES OFTEN
EMPLOYMENT STATUS	# CLOSE FRIENDS *	'OTHER' GROUP *
DWELLING TENURE *	# YRS CURRENT ADDRESS	ENVIRONMENTAL GROUP
AREA SATISFACTION *	# YEARS IN AREA	
BELONG CHILDRENS GROUP **	ENVIRONMENTAL GRP MEMBER **	
GROUP MEMBERSHIP **	PAST COMMUNITY INVOLVEMENT	
AGE X CONFIDANT	PERCEIVED COMMUNITY INVOLVEMENT VERY INVOLVED SOMEWHAT INVOLVED *** NOT TOO INVOLVED NOT AT ALL INVOLVED	
EMPLOYMENT STATUS X CONFIDANT	PAST X PERCEIVED COMMUNITY INVOLVEMENT VERY INVOLVED SOMEWHAT INVOLVED ** NOT TOO INVOLVED NOT AT ALL INVOLVED	
	# YRS CURRENT ADDRESS X PAST COMMUNITY INVOLVEMENT	
% CORRECT 80%	% CORRECT 73%	% CORRECT 74%
SPECIFICITY 82%	SPECIFICITY 69%	SPECIFICITY 56%
SENSITIVITY 63%	SENSITIVITY 94%	SENSITIVITY 81%
rho^2 .19	rho^2 .23	rho^2 .23

*** $p < .001$ ** $p < .01$ * $p < .05$

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THE MULTI-MEDIA APPROACH - CAN ECONOMIC POLICY INSTRUMENTS HELP? by Jack A. Donnan and George Zegarac, Fiscal Planning and Economic Analysis Branch, Ontario Ministry of the Environment. A paper presented at the 1991 TECHNOLOGY TRANSFER CONFERENCE, TORONTO, November 1991

INTRODUCTION

The Ontario Government and other interested constituencies are working together to limit discharges of contaminants into the air, water, and land. However, pollution abatement technologies that reduce discharges into one medium often do so by transferring these contaminants to other media. While environmental professionals have long been aware of this phenomenon and the problems associated with it, administrative structures and legal instruments that have been developed under the Command and Control regulatory paradigm have generally focused on one medium at a time.

Regulatory policy instruments may, in fact, encourage such inter-media transfers or they may be designed to discourage them. This paper reviews the current regulatory framework in terms of how existing incentive structures encourage or discourage cross-media transfers. We then examine how economic incentive policy instruments (i.e. charges, controlled trading, financial assurance, etc.) might affect inter-media transfers. The advantages and the limitations of these policy instruments with respect to the multi-media transfers are highlighted. Comments on how market-based policy instruments might be designed to discourage inter-media transfers are presented.

MULTI-MEDIA AND POLLUTION PREVENTION

The Ontario Ministry of the Environment is developing new regulatory structures and programs that are intended to reduce the discharges and loadings of all types of pollutants into surface waters, the air or to landfill. The Minister of the Environment has articulated three principles which "signal a significant shift in policy for the Ministry of the Environment": pollution prevention, preventing the transfer of pollutants from one environmental medium to another and zero discharge of specific persistent toxic contaminants (Hon. Ruth Grier, Sept. 26, 1991).

Pollution prevention is aimed at inducing all polluters, including individuals and municipal treatment and disposal facilities, to prevent the release of contaminants by substituting inputs that generate harmful waste products for less noxious materials and by introducing process changes or product design changes that will avoid the generation and/or release of contaminants into the environment. Zero discharge will involve absolute prohibition on discharge of certain, yet to be determined, contaminants into any part of the environment by what ever means are effective and acceptable.

End-of-pipe treatment technologies generally transfer pollutants from one environmental medium to another. For example, waste water treatment involves the precipitation, coagulation or filtration of suspended and dissolved contaminants out of water into a sludge that must be disposed of on land or through incineration. Incineration involves the conversion of solids into gaseous residuals and ash. "Scrubbing" of SO_2 and other combustion gasses generates contaminated water and sludges that require land disposal.

Many of the technologies that may be used to comply with existing and forthcoming regulatory requirements will continue to include end-of-pipe processes that transfer contaminants from one medium to another, albeit less problematic, medium or "waste sink" for final disposal.

PREVAILING INCENTIVES FOR INTER-MEDIA TRANSFERS AND TRENDS TOWARD THE "MULTI-MEDIA APPROACH"

For a great many contaminants, the law of conservation of matter implies that inter-media transfers are technically unavoidable once the contaminant is generated by a system or process. Matter cannot be destroyed, only changed chemically or moved physically into more innocuous forms or places. Certain processes or products do not have technically feasible substitutes nor are treatment technologies available to achieve desired discharge reductions without cross-media transfers.

It is also true that waste treatment processes are often designed to discharge residuals to other media in a form or in quantities that permit further natural decomposition and dispersion to harmless levels in the environment. Consequently, cross-media contaminant transfers are not always unintended or detrimental.

Problems arise from inter-media transfers when they are unanticipated or when uni-media regulatory programs fail to curtail potentially harmful exposures of problematic pollutants that occur through pathways via other media. For example, key pathways by which pollutants can affect human health include ingestion of water and/or food, breathing, dermal absorption through contact with water, air-borne particles or certain materials. Containment of the water-borne fraction of contaminants may be of little help in reducing health risks if exposure by air-borne fraction is ignored or increased by inadvertent cross-media transfers.

Inadvertent cross-media transfers may be encouraged by the hitherto traditional focus of regulatory programs and activities on air, water or land. For example, the Ontario Ministry of the Environment is organized into individual branches for solid waste, water resources and atmospheric pollution issues. Existence of the "Water Resources", "Air Resources" and "(Solid) Waste Management Branches in the Ministry of the Environment and other environmental agencies reflects the medium-specific approach to regulation that has prevailed since the creation of the Ministry in 1971.

Environmental guidelines and standards for ambient quality or discharges and effluents are invariably specified in statutes or Regulations for either air, water or land. Moreover, these standards are developed separately by pertinent branches or departments within the environmental agency sometimes using different information sources and often over different timeframes. It is true, of course, that many types of contaminants found in water are not discharged to the air but, for those that are found in air-borne and water-borne phases or are present in soil, standards or guidelines may or may not exist for the contaminant in each phase. Efforts are now being made in most North American jurisdictions, including Ontario, to ensure that standards are set for a given contaminant in all of the phases or media in which it is found. Ontario Environment Minister Ruth Grier (Sept. 1991) has stated that the Ontario Government is committed to "Stopping the transfer of pollutants from one environmental medium to another."

Nevertheless, administrative structures continue to induce branches or departments in environmental agencies to concentrate on initiatives that would maximize the controls, reductions and quality improvements in their own area of concern. For example, the Ontario Environmental Protection Act requires that any person or corporation that builds or operates a facility that discharges, stores, treats or handles waste materials must obtain a Certificate of Approval from the Approvals Branch of the Ontario Ministry of the Environment. Separate Certificates are required for industrial air pollution sources, industrial water discharges and for different types of solid waste handling or landfill disposal facilities. Moreover, the Approvals Branch is organized by individual industrial sections for Air, Waste Sites and Systems, and Wastewater and MISA.

Control documents issued by the regulatory agencies, including the Ontario Ministry of the Environment, often specify requirements for pollutants discharged into a single medium. Control documents issued by Ontario Officials seldom specify overall limits or required reductions of discharges of any source of a particular pollutant from within an establishment or plant. However, as noted, this approach is being reviewed.

Timing differences among major programs that are designed on the basis of air, water or land pollution can also provoke unintended trans-media diversions. Development of water pollution control requirements that precede programs focused on other media will command the initial attention and the available resources of regulated parties to the possible exclusion of controls on pollutants into air or solid wastes. This argument has be raised by regulated firms during various deliberations in Ontario.

Here in Ontario and elsewhere, steps are being taken to develop policies and programs that take account of multi-media problems and issues. Increasingly, policies and programs are being developed with the aid of multi-stakeholder committees and consultations that explicitly consider multi-media implications and make trade-offs where necessary. In addition, the air, water and solid waste management branches in the Ontario Ministry of the Environment are under the purview of the same assistant deputy minister so that mechanisms are in place to take account of multi-media issues and considerations.

Provincial, State and local governments are involved in developing Remedial Action Plans (RAP's) at designated locations around the Great Lakes. The agencies and committees involved in this program are attempting to develop RAP's on a Multi-Media, ecosystem basis to the extent and degree possible. Environmental advocacy groups such as Great Lakes United have recommended the "reorganization of government agencies on a Multi-Media basis" (Great Lakes United, Sept. 1991).

The key point is that limitations on the transfer of pollutants between one medium and another can be established as explicit requirements under the Command and Control regulatory system which can be monitored and enforced.

For purposes of this paper, we define a "Multi-Media Approach" as a two-step process including

- Setting ambient (air or water) quality and/or discharge **standards and objectives** for contaminants that may be found in different media on a coordinated, all-at-the-same time, basis.

- Designing and implementing appropriate **implementation incentive policies** that will establish deterrents and constraints against the discharge or emission of the contaminant in question into all media.

Setting environmental standards and objectives is, and will continue to be, a fundamental element of an effective environmental management strategy. Equally as important is the development of implementation incentive policies that will induce regulated parties to achieve and comply with these objectives in an effective and efficient manner. The focus of the remainder of this paper will be on economic or market-based implementation policy instruments and their potential for preventing undesired cross-media transfers of contaminants.

ROLE OF ECONOMIC INCENTIVE POLICY INSTRUMENTS

Economic instruments have been used in many jurisdictions in the world to assist politicians in meeting their environmental goals. Various types and forms of commodity taxes, effluent charges, extra-strength sewer surcharges, tradeable permits, pollution control delay penalties and assessments and deposit/return schemes are in place or are being considered for implementation in different jurisdictions. The literature on economic policy instruments is large. Useful descriptions of these policy instruments and comparisons of their strengths and weaknesses vis-a-vis the Command and Control regulatory framework may be found in Anderson et al. (1977), Peat Marwick and Partners (July 1983), Donnan (1987) and Dewees (Sept. 1980, 1990).

Economists have generally advocated adoption of one or the other of these policy instruments to enhance and strengthen environmental protection programs in a given jurisdiction. The economic literature on these policy options has emphasized efficiency gains and the increased incentives for timely compliance that contaminant charges, tradeable rights schemes or other economic incentive policies would appear to impart to regulated parties.

The Ontario Ministry of the Environment has investigated these policy instruments over the past 15 years (Donnan and Victor, Oct. 1974); Peat Marwick and Partners (July 1983, April 1989). This work has shown that, to be successfully adopted in the North American regulatory context, economic incentive policy instruments must be designed as **complements** or **enhancements** to existing policies and programs, not as a replacement of the prevailing Command and Control regulatory system. Moreover, each type of economic policy instrument is not necessarily appropriate for each and every environmental problem or issue. New economic policy instruments must be carefully **designed** for specific issues and purposes. Victor (1990) suggests some useful criteria with which the most appropriate type of economic policy instrument may be determined for particular problems or issues.

The question of concern to the present inquiry is whether and how economic policy instruments could affect the unintended and undesired diversion of contaminants from one medium to another. As with Command and Control standards and regulations, economic policy instruments will not prevent unwanted inter-media contaminant diversions if the policy instrument is directed only at uni-media pollutants or sources while ignoring potential releases into other environmental media. Thus, as with Command and Control regulatory elements, economic incentive policies will have to be carefully designed to prevent unwanted cross-media transfers.

There are, however, several features of economic incentive policy instruments which, if combined with the existing environmental policy framework, can be exploited to help off-set undesirable inter-media transfers of contaminants. First of all, if the application of a tradeable rights or entitlements scheme or a contaminant charge program results in substantial abatement cost efficiencies for regulated parties relative to the costs of implementing Command and Control across-the-board reduction requirements to achieve the same degree of discharge reductions, then there will be more funds and resources available for additional expenditures to control potential inter-media diversions.

Another way in which market-based policy instruments may prevent cross-media transfers more effectively than traditional Command and Control instruments involves the application of contaminant charges. The corner stone of a Command and Control regulatory system is the establishment of numerical discharge or ambient quality standards, guidelines or regulations for specific contaminants. These standards are developed on the basis of one of two rationales. First, threshold ambient quality concentrations or pollution loadings values are frequently set at levels which current biophysical data and studies reveal no adverse effects. The other approach is to set discharge contaminant loading "...limits ... based on the use of the best available technology that is economically achievable..." (Ontario Ministry of the Environment, June 1986). The potential for cross-media pollutant transfers arises when information is available to set defensible standards for discharges or ambient concentrations for one medium (ie. water) but not for other phases (ie. air-borne or gaseous) of the same contaminant. Or, as noted, groups within an agency who are developing air-related standards may be ahead of those who are producing water or effluent quality standards. Furthermore, it is often the case that information is only sufficient to develop and defend **guidelines** rather than **legally enforceable standards or regulations**.

Under these circumstances, a polluter will be motivated to devote effort and resources to control the legally enforceable discharges while appropriating less (if any) emphasis and expenditure to control emissions for which only "guidelines" for voluntary compliance are in place. The introduction of a complementary charge on releases of a particular contaminant, whether it is discharged in aquatic, gaseous or solid waste streams from a particular industrial plant, would be an effective method of imposing an on-going incentive to reduce loadings of the contaminant of concern, whether they are subject to "enforceable standards" or to voluntary guidelines or even if there are no specific objectives for the particular parameter. The charge may be applied only to the **excess** of loadings above the specific standards or guidelines or to the **total** loadings being emitted. If charges are applied to the latter, the polluter will have an incentive to reduce all loadings below thresholds defined by standards or guidelines.

Under a comprehensive charge scheme on a specific contaminant, the incentive to redirect contaminants from waste streams with stringent, "legally enforceable" standards to streams with less stringent guidelines or no standards at all would be substantially diminished. Furthermore, once the legality of contaminant charges are established, they could be implemented in a matter of weeks or a few months at most. On the other hand, development of legally enforceable standards, or even guidelines in some instances, often takes years to complete and enact.

When the costs of removing a particular contaminant from one type of waste stream are significantly different from the costs of treatment and removal of the same contaminant from a alternative waste stream that is discharged into another medium, emitters will naturally have an incentive to allocate abatement effort to the lowest cost waste stream and ignore or delay controls of discharges that are more costly to treat and reduce, even if legal standards are in place. Under these conditions, setting standards for one or the other waste streams in ignorance of the relevant abatement cost functions could impose such costly levels of control and abatement that regulated parties would resist compliance and/or initiate unproductive lobbying efforts to get standards changed or mitigated.

Detailed knowledge of abatement cost functions would permit regulators to set total and individual discharge standards for each waste stream that would optimize abatement costs for the regulated plant or facility. However, where there is imperfect information about incremental abatement costs for each type of waste stream, a contaminant charge would induce polluters to implement controls on each waste stream, up to the point where the incremental control costs are commensurate with the charge rate. In addition, a "bubble" standard on all discharges of the contaminants of concern from the plant could be established so that operators could optimize abatement among all sources to achieve the standard at least-cost.

Finally, the Ontario government has enacted a unique policy tool that has important economic incentive characteristics. Part X-A of the Ontario Environmental Protection Act received final reading in December 1986. This legislation empowers the Ontario Ministry of the Environment to require that a regulated party deposit financial security with the Provincial Government as a condition of any legal instrument (ie. order, approval or Regulation) issued by a Provincial Officer. The origins and specific features of the policy are described in Donnan et al. (Nov. 1987).

Provision of financial assurance, as it is referred to in the statute, provides a degree of economic motivation to comply with short-term environmental control program requirements that are specified in a legal control document by specified deadlines. The financial assurance also ensures that funds are available to complete the agreed-to program. Financial assurance is also required to provide funds for future clean-up or rehabilitation of waste disposal sites. Financial assurance is a unique legal provision among North American jurisdictions and, while it eventually must be returned to the regulated party and may not be retained by the government as a penalty, the liability that the financial security imposes on a firm provides an on-going financial impetus to complete agreed-to abatement programs as soon as possible.

Financial assurance is a complementary tool to be used in conjunction with other currently available legal instruments including orders, approvals and prosecutions. By itself, financial assurance would not prevent inter-media transfers. However, where a legal standard or regulations are established that place explicit limits on the discharges and emissions of specific pollutants from all potential outlets or pathways from a particular site, a requirement for financial assurance would give the regulated party an important economic incentive to implement the program.

Careful design of all elements of an environmental management framework, including setting objectives or standards, monitoring and the potential for prosecution, will be required to ensure that cross-media transfers will be reduced or eliminated. Economic incentive policy instruments must also be precisely designed to help in this task. A key design feature would be targeting "multi-media" contaminants for setting objectives, monitoring, application of financial assurance or charges and for the development of cost-effective technical abatement programs.

CONCLUSIONS

Prevailing environmental regulatory administrative and legal structures, program designs and timing of initiatives all contribute to the potential for unwanted and potential adverse cross-media transfers of certain pollutants. The Ontario Ministry of the Environment is committed to "preventing the transfer of pollutants from one environmental medium to another".

Prevention of inter-media contaminant transfers requires the careful design and coordination of existing and new policy instruments. Economic and market-based policy instruments that are being considered by many jurisdictions including Ontario will not, by themselves, realize an automatic adoption of a "multi-media" approach by regulated firms, municipalities or individuals. However, adoption of carefully designed charge schemes, "bubbled" emission requirements or deposit/return schemes such as financial assurance in Ontario, would provide powerful and effective incentives for regulated parties to complete regulatory requirements on time and in a cost-effective manner. Such policy instruments would also help to ensure that funds are available for the required clean-up programs.

The application of economic policy instruments should be viewed as a natural **evolution** of our programs to make environmental management more efficient and effective. They should not be seen as a **revolutionary** change that will replace or eliminate the current mix of tools and instruments. However, because environmental problems have in large measure, economic origins and causes, economic tools and policy instruments are needed to help resolve them.

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ENVIRONMENTAL QUALITY OBJECTIVES REASSESSED[1]

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I. Introduction

A number of pollutants are regulated by setting an environmental quality standard and regulating pollution emissions such that ambient pollution levels do not exceed the standard. The standard is generally uniform across the province or country regardless of local benefits of control. This paper raises questions about the merits and implications of this approach for most pollutants. Evidence is introduced showing that the relationship of ambient pollution concentration to damage often does not provide a solid basis for selecting an environmental quality standard or for defending one level of such a standard in comparison to another. A corollary is that the harm from occasional or modest excursions above such a standard will not usually justify expensive corrective measures. A second corollary is that there may be substantial benefits to be gained from reducing ambient concentrations below the level specified in the ambient standard. These conclusions imply that for at least some pollutants we should search for policy instruments that better serve the actual shape of damage functions that are observed.

This point has received some attention in the economics literature. There is a considerable literature examining the cost of achieving compliance with ambient quality standards using various regulatory instruments. For example, Atkinson and Tietenberg (1982) analyzed the use of marketable permits for achieving an ambient air quality standard for particulates in the St. Louis area, employing an air pollution dispersion model and cost-of-abatement functions for the major particulate sources. They found substantial cost savings from the use of marketable permits as compared to a standard command and control policy, and significant variations in cost depending upon details of the permit system. While they recognize that there may be benefits from reducing emissions below the target level, this crucial fact is not formally incorporated into the analysis. One recent study recognized that reducing pollution concentrations below the ambient standard would generate benefits. Oates, Portney and McGartland (1989) analyzed particulate control in Baltimore. While a command-and-control policy cost $15 million more than an effluent charge policy that achieved the same ambient particulate standard, the net cost of the CAC policy was only $6 million more than for the effluent charge once the benefits of reducing particulate concentrations below the standard were recognized. This study used a benefit function that was linear in concentration, based on a survey of the benefit literature. Portney (1990) discusses problems raised by uniform air quality standards.

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This paper presents a theoretical discussion of individual and aggregate damage functions and the shape of those functions in relation to ambient pollution concentrations. It then briefly reviews the empirical literature on damages for three pollutants: benzene, lead, and sulphur dioxide, assessing the shape of the damage function that is implied. Finally, implications are suggested for pollution control policy.

II. Damage Functions - Conceptual

The problem may be illustrated by considering the shape of the damage function, that is, the magnitude of damage done by various concentrations of a pollutant. For each pollutant, assume that I species of animals and plants may be affected and that there is a population of N_i members of each species. The pollution concentration may vary over time and over location. Assume further that the magnitude of the harm may be expressed in some single index, such as dollars, for any pollutant. While valuation in dollars is difficult, it is not impossible and it allows us to include in a single graph or equation several types of damage that may occur at different concentrations of pollution. For simplicity, three basic individual damage functions will be assessed: the linear, the step function, and the ramp.

A. Linear

Suppose that for a single individual in a species the harm caused by exposure to the pollutant is proportional to the concentration of the pollution. This harm might represent the risk of contracting cancer, or it might represent steadily decreasing crop yield, growth rate, or some measure of function or health. The damage function for the individual is represented by a straight line through the origin, line H in Figure 1. The increment in harm from a one unit increase in concentration, the marginal harm is the derivative of H with respect to C, and is a horizontal line MH.

Suppose that the N individuals in species 1 differ in their susceptibility to this pollutant, so that the slope of their damage functions is different. Suppose further that the I species also differ in the slope of their average damage functions. Finally, suppose that when the maximum concentration of the pollution is C, there are some locations and some times of the year where the concentration is less, but that the concentrations at these other places and times of year is proportional to the maximum concentration. If we aggregate all these damage functions, performing a vertical addition of the curves, we still have a straight line damage function, and a horizontal marginal harm function, shown in Figure 1b. The magnitude of the aggregate harm at a given concentration is of course far greater than that for an individual at the same concentration.

With a linear damage function and a constant marginal harm, choosing an ambient quality standard C* is quite arbitrary. There is no point on the damage or marginal damage function that distinguished itself as desirable. Economists would recommend setting marginal harm equal to marginal cost, so that C* depends on the cost function, which we have not shown. In any event, if an ambient quality standard is chosen, there are benefits from achieving lower pollution levels.

B. Step Function

The opposite extreme from the linear damage function is the step function. Suppose that as concentration increases there is no harm to the individual up to a point C^0, and between that concentration and a slightly higher concentration C^1 some substantial and discrete harm occurs, such as incurring a fixed risk of disease or halting growth, or suffering some specific symptom such asthma. Beyond concentration C^1 there is no further harm. The harm is displayed in Figure 2a for the individual along with the marginal harm, which is zero for most exposures but very high within the narrow region in which the harm occurs. If all individuals were identical and all species identical and all concentrations identical at all times and places then if regulating this substance is justified at all, the only regulation that is defensible is an ambient standard just less than C^0.

Suppose, however, that individuals differ in their susceptibility to this pollutant, so that within a species the concentration where marginal harm is large varies considerably. Suppose that there is even greater variation among species. Finally, suppose that there are variations over space and time in the actual concentration. The aggregate damage curve, as a function of the peak concentration might look like Figure 2b, which shows a uniform distribution of individual damage functions over a wide range of concentrations, giving rise to an irregular total damage function that is approximately a straight line, and a similarly irregular marginal harm function that is approximately a horizontal line. Astonishingly, the assumption of heterogeneous individuals, species, and exposures generates an aggregate damage function similar to that arising from the linear individual damage function. The implications are similar - there is no magic in choosing a particular ambient concentration. Of course, this is a result of choosing a particularly uniform heterogeneity. If the individuals and/or populations were highly clustered or normally distributed, the aggregate damage curves would be more irregular and some sort of threshold might survive as a guide to policy.

C. Ramp Function

The third damage function assumes that at low exposures there is no harm, that there is a substantial range of exposure over which harm increases linearly with exposure, and that there is an upper threshold beyond which no harm occurs. See Figure 3a. This is similar to the step function except that the range of concentrations over which harm changes is large rather than small. Marginal harm is zero except in the ramp area where it is small. Again, assume that the individuals and species vary greatly in the minimum and maximum concentration that causes harm. This will lead to an aggregate damage curve that is similar to that in the second case. If the individual damage functions are uniformly distributed, then total harm will rise monotically, if irregularly, over this range, and marginal harm will be zero at low and high concentrations and while irregular might be represented by an average value in between. If individual damage functions are normally distributed, then total harm will look something like an ogive curve and marginal harm will approximate a normal curve, shown in Figure 3b.

As in the case of the step function, the aggregate damage function will not by itself provide a basis for choosing an ambient concentration standard if the individuals are uniformly distributed. If the individuals are normally distributed and some species dominates, then one would expect that the appropriate standard should be within the upward sloping section of the marginal damage curve. If one had an estimate of the marginal cost of control, one could look for the intersection of marginal cost with marginal harm. Since marginal cost will be a decreasing function of concentration, the intersection is most likely to be in the increasing portion of the marginal damage curve.

III. Damage Functions - Actual

The following brief survey of damage functions is not intended to present the enormous literature that has been produced on each of these substances. It is intended instead to summarize the aspects of that literature that bear on the general shape of damage functions, and to present a preliminary suggestion of the shape that is implied. The underlying literature emphasizes the considerable uncertainty that attends most of our knowledge in this area, and that uncertainty is not reduced by this aggregation and summary.

A. Benzene

The principal concern arising from environmental exposures to benzene is an increased risk of cancer, specifically leukemia. (MOE, 1990, pp. c-19 to 21.) Since dose-response functions are estimated from populations that faced high occupational exposures, there is uncertainty about risks at low doses. It is generally assumed, at least for regulatory purposes, that the risk is proportional to exposure, with no safe threshold, although this may over-estimate risks at low exposures. This yields a linear risk or damage function and a constant marginal damage function, as shown in Figure 1a.

The summary literature does not indicate differences in susceptibility to cancer among humans, nor does it indicate risks to other species. However with the linear dose-response model even if such differences occur, the aggregate damage function will still be linear through the origin, and the marginal damage function will be constant, as shown in Figure 1b.

Benzene appears to fit the linear model of Figure 1 perfectly, at least within the limits of current knowledge. This implies that if an ambient standard is employed, a given quantum of reduction in concentration below the standard are neither less nor more valuable than the same reduction above the standard.

B. Lead

The introduction of lead into the environment gives rise to several concerns including human health effects and possible future harm to ecosystems as lead accumulates in water, soil and the food chain. The evaluation of lead risks is complicated because as a persistent heavy metal it accumulates; there is a slow accumulation of lead in the body as a result of respiration, ingestion and excretion over time, and a slow accumulation in the environment as a result of airborne deposition, but without significant natural removal mechanisms. Most human health effects are measured in relation to blood lead levels, not environmental concentrations.

In humans, lead gives rise to a variety of symptoms and problems at varying blood lead levels. The USEPA (1986, pp. 1-142 to 1-153) reports a variety of such effects and the exposures at which at least some persons have been observed with the effect. For children, these effects begin at exposures of less than 10 μg/dl with increasingly severe effects occurring up to 80 μg/dl; death may occur from exposure to 80-100 μg/dl. For adults there is a somewhat different list of effects beginning at about 10 μg/dl and rising again to about 80 μg/dl. Dose-response graphs show effects that are linear in blood lead concentration, log-linear, and ogive. While the importance of some of the symptoms is not obvious to someone without medical training, the clear picture from this evidence is of harm that may be zero at blood lead levels of 1 μg/dl and rising monotonically until at levels of 80 or 100 there is a risk of fatality for at least some individuals. Furthermore, the literature implies that individuals vary in their susceptibility to lead damage, so the range from no effect to serious effects for all humans would be much broader than this. Finally, the EPA notes that airborne lead emissions probably contribute 25 to 30 percent of the blood lead in persons living in industrial areas.

This evidence on human health effects suggests that for exposed populations there may be a "safe threshold", but there is a considerable range of airborne concentrations over which more is worse and less is better, without any particular concentration at which a small increase causes particularly large aggregate harm. In short, this may be like the ramp function of Figure 3.

The Ontario MOE (1990, p. c-89) does not indicate harmful effects for species other than humans at current ambient concentrations. The tendency to accumulate in the environment may mean that in the future harm could arise from further accumulation. If so, it seems likely again that damage would occur first to individuals and then to species, and that the benefits of a reduction in emissions now would be to postpone the date when such harm might occur. This suggests a linear damage function, perhaps with a non-zero intercept.

C. Sulphur Dioxide

Sulphur dioxide is not a carcinogen, but chronic inhalation may give rise to health effects in humans. While the evidence on these effects is not satisfactory, some tentative conclusions have been drawn. The USEPA (1982, p. 1-105) concludes that respiratory symptoms and pulmonary function decrements may occur in children for exposures above certain levels, but that the risks at average ambient sulphur dioxide concentrations are likely nonexistent or minimal. The MOE (1990, p. c-155) states that there may be no risk of fatality arising from sulphur dioxide exposure, but on the other hand there may be a risk that is linearly related to concentration; linear risk equations are also presented for hospital days for respiratory conditions and for hospital admissions for respiratory disease. Taking these two reports together I conclude that there may be no effects at low exposures but that there is a range of exposure where health effects may be linearly related to exposure. Aggregating across individuals would yield something like Figure 3b.

The MOE does not list other effects except there is a threshold for phytotoxicity at 0.02 ppm. The USEPA (1982, p. 1-35) concludes that for any plant species there is a threshold concentration above which injury will occur, and that this threshold varies with each plant species and with other environmental conditions. There is no suggestion that exposure above the threshold will be fatal; instead there is some visible damage. Plants may recover from short fumigations, so the duration of exposure matters. This suggests a damage function rather like that of Figure 3.

Finally, there is the acid rain problem. While soils and lakes may have a buffering capacity, their capacity to absorb acid varies enormously. In any given lake or ecosystem that is beyond this threshold there is a range of precipitation within which more is worse and less is better. Combining these factors suggests individual damage functions like Figure 3a and an aggregate acid rain damage function like Figure 3b.

Combining human and plant effects should yield an aggregate damage function like that of Figure 3, with a broad range of exposures within which small increases cause small increments in harm.

IV. Conclusions

In the case of several pollutants, both theory and evidence reject aggregate damage functions that are discontinuous, with enormous harm occurring as a result of a small increase in pollution discharge. If the effect of a pollutant on an individual is an increasing function of exposure, and if individuals within a species differ in sensitivity, and if various species differ in sensitivity, then the aggregate damage function must increase gradually but monotically over a wide range of exposures as in Figures 1b, 2b, and 3b. These damage functions do not display a discontinuity or step in aggregate damages that would offer an obvious guide to an environmental standard. In this situation, some consideration of costs and benefits offers a means of determining the standard.

It seems likely that for many pollutants, including all three of those studied here, any defensible ambient standard will be set such there are some benefits from control below the standard, and benefits from control above the standard, and the marginal benefits per unit of control may not differ much in the vicinity of the standard. This suggests that there may be considerable merit in treating such standards flexibly, and pressing for abatement below the standard when this is not too costly, and allowing some excursions above the standard when this is not too harmful.

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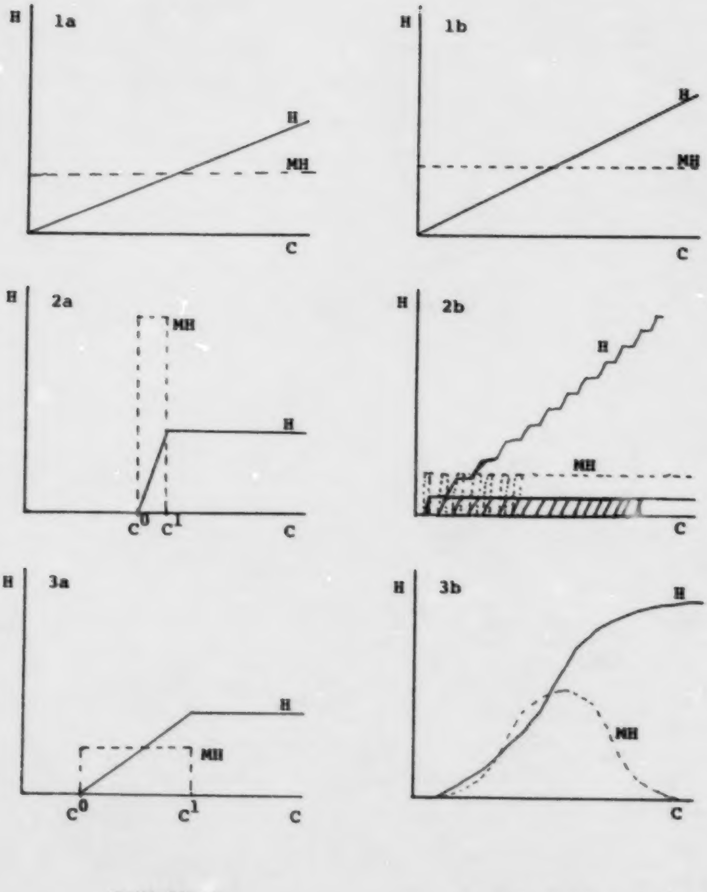
FIGURES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Individual Aggregate

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EVALUATION RESEARCH FINDINGS AND ENVIRONMENTAL POLICY CHOICES

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Putting dollar values on environmental losses -- on degradation of scenic amenities, destruction of wildlife habitat, erosion of beaches, increased risks of toxic spills, deterioration of air quality, and the havoc resulting from oil spills -- has recently moved from the domain of a few academic studies to the basis for determining damage awards in environmental litigation and attempts to settle increasingly acrimonious disputes over the siting of environmentally disruptive activities and the use of environmentally sensitive resources. This has prompted a rash of evaluation studies to satisfy this new demand, and it is now increasingly commonplace to see reports indicating, for example, that "state residents ... indicated they would pay up to $10 per bird for protecting them from future [oil] spills" (The Seattle Times, 14 December 1990). The stakes are far from trivial, for both parties facing compensation claims based on such estimates, and for communities choosing between serious curtailment of economic activity and environmental disruptions.

While monetary estimates of environmental values have occasionally found their way into benefit-cost analyses and have sometimes been cited to gain support for particular environmental policy proposals, the new-found enthusiasm to assign dollars to non-pecuniary losses stems from recent legal and policy requirements. The most notable among these is the Comprehensive Environmental Responses, Compensation and Liability Act (CERCLA, or Superfund) in the U.S, making polluters liable for not only the costs of cleanup, but for "damages for injury to, destruction of, or loss of natural resources". A similar trend seems evident in Canada where litigants are also pursuing a damages remedy for environmental losses, preservation and development options are being assessed, and the Ontario Law Reform Commission has recently recommended "the creation of a new civil statutory remedy, an award of damages payable to compensate the public for harm done to the environment, entirely independent of any damages payable for injury caused to individuals or corporations" (Ontario LRC, 1990, p. 2).

In essentially all of the studies or regulations, estimates of people's willingness to pay to avoid whatever environmental loss is at issue are used or ordered; and increasingly contingent valuation surveys are used or prescribed, in which samples of respondents are asked to state their valuation of the loss in terms of their willingness to pay to avoid them.

However, despite growing practice and optimistic reports to the contrary, the empirical evidence strongly suggests instead that (1) the use of the willingness-to-pay measure is likely to be highly inappropriate, and (2) the interpretation of contingent valuation as measures of economic values may be incorrect and seriously misleading. While studies using contingent valuation methods (CVM) to estimate willingness-to-pay (WTP) values, are almost guaranteed to produce numbers -- which may be one of the problems -- on present evidence, there seems to be little or no justification for using the estimates to assess compensable damages or to allocate resources between conflicting uses. There is no empirical support for such practices and there is persuasive evidence that numbers produced by CVM studies to assess WTP values of losses will seriously distort environmental policy choices.

The Valuation Disparity

The problem with the use of the willingness-to-pay measure is that it is the basis for assessing gains rather than losses and while it is conventionally assumed to be equivalent to the more appropriate compensation demanded measure of loss, and therefore an adequate substitute, this assertion now appears to be seriously in error.

Studies and environmental assessments continue to be carried out with the apparent expectation that any disparity between the willingness-to-pay (WTP) and the compensation-demanded (willingness to accept, or WTA) measures will be negligibly small and of no practical importance -- that "according to utility theory, the amount subjects would be willing to pay to clean up a site should be the same as the compensation they would be willing to accept to allow someone to pollute the site (apart from a minor income effect)" (Phillips and Zeckhauser, 1989, p.527). As a result, it has become common practice to base assessments of environmental losses on this presumption of evaluation equivalence. No reckoning of any difference is made, or thought to be necessary, and the more conveniently measured WTP has, as a result, become the measure of choice.

There is, however, little evidence to support this traditional view of equivalence, and the consequently easy presumption that WTP measures adequately measure the value of losses -- environmental or others. Instead, the available evidence, which has been accumulating for a dozen years or so, supports an alternative view of large and systematic disparities. The results of the many controlled tests of the equivalence proposition are consistent in showing that losses matter much more to people than commensurate gains; and that reductions in losses are more valuable than foregone gains. These differences have been shown to be independent of transaction costs, repetition of trade offers, income effects or wealth constraints (Kahneman, Knetsch and Thaler, 1990). Research studies consistently find that people require payments to give up entitlements that are from about two or three to well over five or ten times larger than the maximum sums they would agree to pay to retain the same rights -- with the disparities for environmental losses typically at the higher ranges. The findings suggest that attempts to assess environmental losses will be severely hindered by continuing to ignore the differences.

While these findings have until recently not proven popular with many economic practitioners and assessors of environmental losses -- an unfortunate social cost of the reluctance to give up conventional assertions -- they seem in accord with the strong intuitions of most people. A particularly persuasive illustration of the differing valuations of gains and losses has recently been provided by responses to recent automobile insurance legislation in the states of New Jersey and Pennsylvania in the U.S. Both states introduced options that allowed people to choose between cheaper policies that limited rights to subsequent recovery of further damages and a more expensive policy permitting such actions. Importantly, the default option differs between the two states, with the reduced right offered in New Jersey unless it is given up and full rights are given in Pennsylvania unless the less expensive option is specified. Given the minimal costs of choosing either option in both states and the large amounts of money at issue, the results have been dramatic: to date over 70 per cent of the New Jersey auto owners have adopted the limited right, but less than 25 per cent of Pennsylvanians have done so (Meszaros, et.al. 1991).

If the valuation differences represent the general case, as the evidence now suggests, then the usual assumption of equivalence between gains and losses will be a poor predictor of people's behaviour and of their judgments of the fairness and acceptability of environmental policies (Kahneman, Knetsch and Thaler, 1986a and 1986b; Knetsch, 1989). Assessments based on the equivalence assumption will likely result in: serious under-statements of losses, undue encouragement of activities with negative environmental impacts, underassessment of compensation and damage awards, setting of inappropriately lax standards of protection against injuries, inadequate mitigation measures, biasing of choices of preferred legal entitlements, and devoting too few resources to avoiding environmental harms (Knetsch, 1990).

Distinctions between gains and losses, and on whether a positive change is taken as reduction of a loss or a gain, and a negative change is perceived as a loss or a foregone gains, which to a large extent determines the desirability of changes or acceptability of proposed resolution of conflicts, are not necessarily determined by either the status quo or extant legal entitlements. Reference positions may well be based instead on an expected or normal condition, which may differ from the present and from legally enforceable rights. Reducing current pollution levels, for example, may be viewed as a reduction of a loss from a reference of a clean environment and therefore worth more than as an improvement from present levels of degradation. Reference levels may also be induced in some circumstances, by defining a widely acknowledged "acceptable" level, or "objective standard". The use of "poverty lines" in jurisdictions throughout the world is a notable example of the success of such a strategy even though such income levels are widely known to be little more than arbitrary designations. Environmental standards often serve a similar function in defining gains and losses -- and distinguishing between gains and reductions in losses.

A further example of likely bias toward inefficient environmental policies resulting from the assertion of equivalence in the valuation of gains and losses is in choices between mitigation measures that eliminate or reduce environmental harms and compensation payments that permit injured parties to make up for the loss by substituting other goods or resource entitlements. The usual economic analyses and prescriptions indicate that people would usually be made better off with a cash remedy that does not restrict purchasing whatever is most valued by the recipient rather than having a like sum devoted to the restricted use of mitigating the injury. However, the gain/loss disparity findings suggest that mitigation measures might be valued more because they reduce losses, and compensation awards might be heavily discounted by being in the domain of gains.

The results of a series of empirical studies appear to be consistent with the different weighing of gains and losses. In one extensive series of telephone surveys, respondents in the Toronto area were asked one of four versions of the following question:

> Suppose a newly opened gravel pit causes sediment to flow into a local stream and that this reduces fish populations by about 10 per cent. The amount of sediment can be reduced by half if the company spends $200 000, but everyone agrees that no amount of money would eliminate the problem. The company offers to either spend $200 000 on reducing sediment, or to give the same $200 000 to ________X________. Given that the money will be spent on one or the other, which would you prefer?

The alternatives to spending on reducing sediment, the X in the question, were (1) to have the money put into the general fund of the province -- arguably the most efficient policy, (2) paid to the general fund of the local municipality, (3) to the local parks and recreation authority for use in whatever project is most desired by the community, and (4) spending the money to increase other fish populations -- an attempt to provide a closer substitute for the losses suffered. Even though the question was purposely designed to suggest a fairly minor loss with little that could be done to mitigate the harm, a majority of the respondents in each case said that they would rather have the resources devoted to this than to a seemingly attractive alternative:

Spend on		Spend on Mitigation
Province general fund	15%	85%
Municipal general fund	19%	81%
Parks/recreation	32%	68%
Other fish populations	27%	73%

Some variation of preferred remedy was evident in the responses, with putting the money into either the provincial or municipality general fund clearly the least satisfactory remedy. But even the seemingly close substitute of increasing other fish populations was rejected by over two-thirds of the respondents. Reducing losses, even small increments to minor ones, appear to be more important to people than a gain in other desirable facilities.

The survey findings and the valuation disparity that seems to give rise to them, suggest that more attention to remedies may well be in order. The often proclaimed directive to "pay off the losers" as a means of "making them whole" and to eliminate opposition to various projects and activities, seems to be an expensive and ineffective remedy. The form of remedy may be better tailored to the various perceived dimensions of loss to be most effective. This might take the form, for example, of determining what attributes, or dimensions, of a loss people representing various interests view as being effected by the change and designing remedies that closely offset the adverse impact to each. Remedies designed in accord with people's actual preferences are likely to be not only more effective, but to be far more efficient -- less money will be needed to make people better off than with more traditional approaches.

Contingent Valuation Methods and Embedding

The demand for assessments of non-pecuniary environmental values has motivated the development and now extensive use of contingent valuation methods (CVM). The essential feature of these techniques is that people are asked to nominate a sum of money that would make two hypothetical conditions, or contingencies, equally attractive or equivalent to them. A typical form is to ask a sample of respondents for the maximum amount they would be willing to pay to have a new park provided for their use -- the sum that, if they paid it, would leave the individuals indifferent between having the park with the diminished wealth and not having the park while maintaining their present monetary position. The estimates yielded by responses to CVM questions have been widely taken as expressions of economic values that are fully comparable to the assessments of what people are willing to give up that are measured by market prices.

While applications of the CVM has been extensive -- in part due to the assurance that specific estimates are always produced -- violations of the presumed comparability between CVM estimates and market values have been noted in some reports, although often in passing. There has, for example, been some concern with evidence suggesting that estimates of WTP for a public good are strongly affected by its position in a list of goods for which WTP is elicited; the same good will elicit a lower WTP if it is down in the list than if it is the first (Mitchell and Carson, 1989).

CVM values are also frequently subject to anchoring effects that should not have any noticeable influence on valuations that truly represented respondents' willingness to sacrifice in order to acquire or maintain an entitlement. For example, in one series of telephone interviews the proportion of adult Toronto householders saying they "would personally favour a $50 increase in your tax bill to prevent a [described] drop in fish populations in the Muskoka region of Ontario" varied from 19 per cent for those who were first asked if they would be willing to pay $25, to 66 per cent for those first asked to pay $100. This large difference indicates a strong influence of whatever number is suggested first and suggests that the resulting CVM valuations do not share the trade-off characteristic of market values.

Finally, and perhaps most importantly, there is now also evidence of what has become known as an embedding effect (Kahneman and Knetsch, forthcoming), also variously labeled as a part-whole effect, symbolic effect, or disaggregation effect (Cummings et al, 1986; Mitchell and Carson, 1989): the same good is assigned a lower value if WTP for it is inferred from WTP for a more inclusive good than if the particular good is evaluated on its own.

In an earlier study, Toronto residents were asked if they would be willing to pay $50 in increased taxes "to prevent the drop in fish populations" in more or less inclusive areas of Ontario. The proportions willing to pay this sum for the fish in all of Ontario was only slightly higher than the willingness to pay to preserve the fish stocks in only a small area of the province.

A subsequent survey of three samples of Vancouver residents demonstrated an even higher degree of embedding for two largely public, but otherwise dissimilar, goods. One group of respondents indicated that they would be willing to pay an average of about $22 each per year "to maintain the current fish populations in the northern interior of British Columbia." A second group said they would pay an average of about $20 to "preserve historic buildings throughout British Columbia. The third group suggested that they would be willing to pay a total of $21 per year to save both the fish in northern B.C. and the historic buildings throughout B.C.

A further study of adults living in the greater Vancouver region was carried out to investigate the embedding effect in the context of public goods readily recognizable by respondents (Kahneman and Knetsch, forthcoming). The median amounts that respondents said they would pay for "equipment and trained personnel" to deal with environmental emergencies varied from $25 when that good was evaluated on its own to $1 when the initial question concerned WTP for a longer list that included this subset. This suggests that in this and all cases in which such effects are present the valuation of a good will vary depending on the level at which the good is embedded. In such instances measures of environmental losses and compensable damages using CVM are largely arbitrary and lack comparability to the economic value of alternative resource uses.

If embedding is present in survey responses, then any single estimate would be too arbitrary to provide either a basis for legal actions for damages or a useful guide to resource allocation policies. For example, if the value of a group of sea otters varies by a sizable multiple depending on whether the assessments are derived from people's responses to being asked about all otters, all sea mammals, or a single otter, then there is little in these answers that will either accurately assess the compensable loss for the destruction of any specific number of sea otters or provide an appropriate basis for determining what resources should be devoted to avoiding such losses.

The major implication of these findings, and the consistent evidence reported by others, is that given the possibility, and on present evidence the high likelihood, that embedding might be found in assessing the value of a particular environmental good, it is necessary to demonstrate that embedding is not present in the valuation of that particular good or entitlement. Without such a finding, any assessment based on CVM would remain suspect and justifiably subject to easy dismissal.

The results do not necessarily imply that the valuation of every good is susceptible to an embedding effect. They do, however, indicate that in the absence of demonstrations that these problems are avoided in specific applications, continued reliance on CVM on grounds of a lack of viable alternative assessment methods is unwarranted, as is the often stated potential of CVM to yield appropriately reliable and useful measures of the economic values of public goods to determine compensation for environmental losses and efficient allocations.

Conclusions

There seems to be little empirical evidence to support the increasingly common practice of assessing environmental losses by CVM surveys asking questions about people's willingness to pay to avoid them. Assessing environmental losses remains contentious, but the current practices may well be failing to improve either the efficiency or equity of remedial measures.

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VOLUME I

SESSION C

ENVIRONMENTAL MANAGEMENT OPTIONS

POSTER PRESENTATIONS

CP1

Experimental Study of the Guelph Pilot-Scale Solid Waste Composter

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The Ontario government has set goals to reduce the amount of waste disposed in landfills by 25% by 1992 and 50% by the year 2000. In May 1987, the City of Guelph (pop. 80,800) began a citywide residential blue box recycling program as a first step to divert MSW from its rapidly filling landfill. However, even after including apartments, townhouses, businesses and institutions, the total diversion rate was still below 10%. The second step was to consider composting of all organic waste and a pilot program was developed to study source separation and collection of dry and wet waste. The wet or organic waste was to be composted.

Three groups of homeowners were selected to participate in the project. Each group, consisting of 200 households, was assigned one of the following three methods of separating the waste:

Three Stream (Group A)	- wet waste (compostable) in green bin (120 l) - recyclable dry waste in blue bin (240 l) - non-compostable and non-recyclable waste in regular garbage containers
Two Stream (Group B)	- wet waste (compostable) plus sanitary napkins, disposable diapers, ashes/coals and contents of vacuum cleaner bags in green bin (120 l) - all dry waste in regular garbage bags
Two Stream (Group C)	- wet waste (compostable) plus sanitary napkins, disposable diapers, ashes/coals and contents of vacuum cleaner bags in green bin (120 l) - all dry waste in blue bin (240 l)

The wet (compostable) material includes all food scraps (vegetable and fruit peeling, meat and bones, fats and cooking oils, egg shells, dairy products, coffee grounds, filters and tea bags, and food leftovers) and yard waste (brush, grass clippings and leaves).

Almost all available data on mixed-waste MSW compost from the U.S. and Europe indicate that the limits on cadmium, chromium, copper, lead, mercury, and zinc cannot be achieved on the average. Data for the very few U.S. and European projects dealing with source-separated organics and yard waste show that most of the limits may be achievable. However, most of the data greatly exceed the mercury limits, often by a factor of 10. In any case, both Ontario and British Columbia are proposing regulations to encourage source separation of MSW, thus eliminating such options as co-composting sewage sludge and MSW.

The objective of this paper is to describe the Guelph pilot composting system and to compare the quality of the product with the Ontario Ministry of the Environment's draft guidelines and British Columbia Ministry of Environment's proposed standards.

A 10 tonne/week pilot plant was constructed at the landfill site to compost the wet stream of groups A and C. The composting facility, which is shown schematically in Figure 1, is a hybrid between a static aerated pile and an in-vessel reactor. The primary cells are 3m x 3m and the secondary cells are 4.5m x 3m. Both are normally loaded to a depth of 1.2m.

Kitchen waste is sorted manually from the yard waste at the site. Metals and plastics are removed and sent to the recycling plant. All oversized organic materials (except tree branches) are manually cut into smaller pieces. All excess yard waste is stockpiled for future use and oversized branches are put through a wood chipper. The proportions of kitchen waste, yard waste, wood chips and mature compost are adjusted to attain a C/N ratio of about 30. Wood chips are used as a bulking agent and mature compost is spread on the surface of the pile for fly control. Waste is kept in the primary cells for three weeks and

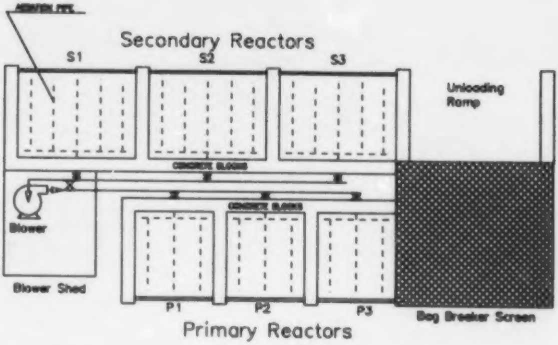

Figure 1. Top view of the Guelph Pilot MSW Composting Facility

five or six weeks in the secondary cells. The contents of two primary cells are used to fill a secondary cell. After week 9, the fresh compost is unloaded from the secondary cell, screened and windrowed for another five weeks for stabilization.

Airflow to each cell is controlled by timers and manual valves in the pipe leading to the cell. Every 6 hours, the airflow direction is changed from blowing to suction. The duty cycle of the blower is set at 33% to provide 5 min. of continuous fan operation for each 15 min. interval, and all manual valves are opened fully.

The moisture content of the composting mass is checked daily. During the first six weeks of the composting cycle, the moisture content is kept at about 65% (w.b.) by adding water or leachate. In weeks 7 through 9, the moisture content is allowed to drop to 35%.

Three samples of each batch of fresh and matured compost are analyzed for total carbon content, total nitrogen content, nutrient contents, volatile matter content, dry matter content, pH and heavy metal contents (cobalt, cadmium, chromium, copper, manganese, nickel, lead and zinc).

Pile temperatures are monitored with a probe which has three thermocouple sensors, 300 mm apart, so that the pile temperature can be monitored at 300 mm, 600 mm and 900 mm above the cell floor. A data acquisition system samples the temperatures at 60 s intervals and stores hourly averages for analysis.

About 50 batches have passed through the system and the results of batches 21 and 22 are presented for illustration purpose. These batches were put into the primary cell on August 15 and 22, 1990, respectively, and combined in the secondary cell on September 11. The compost was moved to the windrow on October 16.

In order to check for the achievement of sanitizing temperature-time condition during the process, the temperature history obtained with seven distributed probes in the secondary cell (aerated-static pile) was compared with several sanitizing temperature-time criteria. The criteria used in order of preference are:

1. 55°C to 60°C for 15 consecutive days; or
2. 70°C for 30 minutes; or
3. 65°C for several hours.

Fresh compost was considered sanitized if either one of the three criteria is achieved. It was observed that the temperature-time conditions matching criteria 2 and 3 occured several times during the process, and only the last time was considered as the sanitizing condition. The results indicated that the fresh compost of the mixture of batches 21 and 22 was sanitized at all temperature-monitoring locations.

Samples of mature compost were tested for such pathogens as faecal streptococcus, faecal coliform, and salmonella. The results showed 290 counts/g for faecal streptococcus, 500 counts/g for faecal coliform, and 0 counts/100g for salmonella. The low counts indicate that the material was indeed sanitized.

The compositional analysis of mature compost is shown in Table 1 along with the Ontario Ministry of the Environment's Draft Guidelines and the British Columbia Ministry of Environment's Draft Regulations. Most quality parameters are within the limits set by those standards. With the exception of mercury concentration, the heavy metal concentrations are well below the specified limits. The mature compost is also rich in organic matter and plant nutrients. This particular analysis is representative of the analyses obtained for other batches.

Table 1. Compositional analysis of Guelph's Mature Compost

Parameter	Guelph's MSW Compost	Ontario Draft Standard	B.C. Regulation Code 1
Cadmium (1)	0	≤3	≤2.6
Chromium (1)	22	≤50	≤210
Cobalt (1)	2	≤25	≤26
Copper (1)	26	≤60	≤100
Lead (1)	40	≤150	≤150
Manganese (1)	347	-	-
Nickel (1)	13	≤60	≤50
Zinc (1)	134	≤500	≤315
Arsenic (1)	3.2	≤10	≤13
Mercury (1)	0.19	≤0.15	≤0.83
Molybdenum (1)	<2	≤2	≤7
Selenium (1)	0.2	≤2	≤2.6
Total N (2)	1.3	0.6	-
Total P (2)	0.3	0.25	-
Total K (2)	0.7	0.20	-
Total Ca (2)	8.9	3.0	-
Total Mg (2)	3.6	0.3	-
Total Salts (3)	2.3	<3.5	<2
SAR	0.2	<5	-
Org. Matter (2)	34.1	30	≥20
Moisture (4)	34.0	30-55	≤50
pH	7.6	5.5-8.5	5-8
WHC (2)	110	300	-
Total C (2)	22.3	-	-
Ash (2)	65.9	-	-
Initial C/N			
Batch 21	33.6		
Batch 22	25.8		
Final C/N			
Batches 21&22	17.2	22.0	-
Org. Reduction (%)	77	NS	-

(1) unit in ppm
(2) unit in percent dry basis
(3) conductivity, unit in mS/cm
(4) unit in percent wet basis
NS no limit specified
- not required or not analyzed

CP2

MODELLING MUNICIPAL WATER SYSTEMS FOR DEMAND MANAGEMENT

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INTRODUCTION

Traditionally, municipalities in Ontario and across Canada have practised supply management (Kreutzwiser & Feagan, 1988; Brooks & Peters, 1988). This approach views any forecast increases in demand for water as goals to be met by increasing the available supply capacity. Demand management, by contrast, attempts to modify the amount of water used, so that expensive and resource intensive expansions of water supply capacity can be delayed or avoided.

The goal of this study is to produce a forecasting model for the use of water managers that can evaluate a selection of demand management options. The example in the model is the water system of the Regional Municipality of Waterloo. This is particularly appropriate, because in this Region a major expansion of water supply is under way, and because of administrative complexity, as there is a division of jurisdiction between the Regional and local municipalities. Water conservation programs can be different in each municipality.

The model has focussed on water fixtures and on pricing, two areas where the Regional Municipality of Waterloo has also taken an interest. The Region has made retrofitting devices for water fixtures available free on demand for a number of years. Toilet dams, faucet aerators and showerhead flow restrictors are among the devices supplied. In the past year in the City of Waterloo, retrofitting kits were distributed door-to-door with a follow-up questionaire. To date, the Region has not used pricing as a demand management tool, although a consultant to the Region has investigated this (Koehler et alia, 1989).

Modelling was done on a Macintosh SE/30 using as software a combination of STELLA, a general systems modelling application, and Apple's HyperCard. More information on the software used has been presented previously (Creese & Robinson, 1990).

WATER FIXTURES MODULE

Based on input data, this module calculates the numbers of housing units with retrofitted water fixtures and with conserving water fixtures for each modelling year. Figure 1 gives a sample of this output. The module then calculates the resulting water savings by year.

The yearly requirements for new fixtures, whether normal or conserving, and for new retrofits are additional outputs of this module. The resulting tables of requirements for new conserving fixtures and new retrofitting (see Figure 2) are useful in determining the cost of relevant municipal programs. Calculation of these requirements is a non-trivial exercise, since municipal programs, changes in population and changes in number of people per housing unit are not the only driving forces (see Table 1). During each year, both fixtures and fixture retrofits are retired and replaced (or not) due to normal wear and tear. Thus, using the example given in Figures 1 and 2, new retrofitting must be provided for 221 housing units in order to go from 1,269 retrofitted units in 1988 to 1,264 retrofitted units in 1989. In addition, certain municipal programs may contribute to early retirement of normal fixtures and their replacement by conserving fixtures.

Information is required on the initial proportion of housing units which already have been retrofitted and on the initial proportion of conserving units. A population forecast for the municipality and a forecast of the number of persons per household are also required. Survivorship curves are required for the various types of fixtures and retrofitting. These in general have to be estimated, based on the limited amount of information that is available from manufacturers.

Municipal water conservation programs are defined in the Water Fixtures Module by means of program parameters: water saving per housing unit, consumer acceptance rate and the fraction of the municipality targetted. Programs are input into the module via program selection charts (see Figure 3). As an example, with respect to retrofitting, one municipal program might be to simply make retrofitting kits available to home-owners on request, another might be door-to-door distribution of kits with a follow-up phone call. Obviously, these two programs would result in very different acceptance rates. The Water Fixtures Module contains default programs for retrofitting, for the installation of conserving fixtures in new housing units and for the replacement of normal fixtures by conserving fixtures. The user can select from these default programs or construct his own by typing in different program parameters.

PRICING MODULE

The pricing of water is important, since price is one factor determining the level of water use (Howe & Linaweaver, 1967; Prasifka, 1988). Different uses for water are differently affected by price. Howe & Linaweaver (1967) established that the outdoor use of water in summer by residential users is more affected by price than is indoor residential water use. This is a finding of primary importance, since it is the high water use of summer that causes the greatest demand for water supply augmentation.

In this module, we have adopted the principle of full cost pricing. This means that water system costs are paid for by water consumers, with no subsidy from general taxation. Implied in this philosophy is that the sale of water should be revenue neutral. In practice, a water utility operation may have costs which vary tremendously from year to year, particularly capital costs. To prevent corresponding year to year fluctuations in price, price smoothing may be employed. Full cost pricing in the context of price smoothing implies the water utility system may not be revenue neutral in a particular year, but must remain so on average over a longer period. Full cost pricing and price smoothing are both presently policies of the Regional Municipality of Waterloo.

The Pricing Module uses full cost pricing, combined with a ten year smoothing period, to calculate an average water price for each year. However, the Pricing Module also sets a higher price for the summer period. The rationale is that a higher summer price better reflects the higher costs of providing water for summer uses. It also may depress summer use and delay the need for supply augmentation. Since it is the higher summer use that necessitates system expansion, a higher summer price is equitable.

In the Pricing Module, water use was divided into three components: base (winter) use, summer excess use and peak day use. This enables a different price elasticity of demand to be applied to each. Since much of summer excess water use is outdoor use, such as lawn and garden watering, summer was defined as those months when there has historically been a climatic moisture deficit (May to October inclusive). The meaning of the terms 'base use', 'summer excess use' and 'peak day use' can be illustrated using the historical averages from the Regional Municipality of Waterloo. The average annual use was 100 gal/person/day and the average summer use was 105 gal/person/day, giving a summer excess use of 10[1] gal/person/day and a base use of 95[2] gal/person/day. Annual maximum day use averaged 150 gal/person, giving a peak day use of 45[3] gal/person/day.

The Pricing Module establishes a price for summer excess use. Since the average price is already established by the principles of full cost pricing and price smoothing, the two prices that would actually be charged to the consumer, the base price and the summer price, can then calculated. Since the average price remains constant, the higher the summer price, the lower the base price.

For example, using the historical water use values given above, and assuming for the sake of easy calculation that price does not affect water demand, consider two cases in which the average price is $1.00/100 gal. If the summer excess use price is $2.00/100 gal, then the two prices charged to the consumer would be: base (winter), $0.95/100 gal and summer, $1.05/100 gal. If the summer excess price were increased to $5.00/100 gal, then the winter price would be $0.79/100 gal and the summer price, $1.19/100 gal. However, the Pricing Module does assume that price affects demand, so that the actual calculations are much more complex. For a given average price, a higher summer price should bring about a slight increase in base use, a proportionately larger decrease in summer excess use and an even larger decrease in peak day use.

The method of establishing the price for summer excess use has not yet been stabilized; several methods are under consideration.

INTEGRATING THE MODULES

In applying the two modules to water use forecasting, it is conceivable that the modules could be used consecutively or concurrently. If mutual feedback is required between the two modules, the concurrent option would be necessary.

Water conservation programs modelled in the Water Fixtures Module will affect base water use, though not summer excess use or peak day use. This reduction in use must be known in order to successfully apply the Pricing Module.

The Pricing Module also has some possible effects on the Water Fixture Module. In theory, different price elasticities should apply to housing units which have retrofitted or conserving water fixtures. There is also the possibility that higher water prices might motivate people to retrofit their fixtures or acquire conserving ones. Water prices are presently so low that these effects were judged to be minimal and were discounted.

---

[1] (12 months/6 months) x (105 - 100)

[2] 105 - 10

[3] 150 - 10 - 95

The two modules therefore can safely be run sequentially, with the Water Fixtures Module run before the Pricing Module.

DISCUSSION

The model should be very useful both to consulting firms and to municipalities. While many people are aware of the concept of demand management, the application to water supply and wastewater treatment planning is not well understood at present. In addition, a further study to determine the effect of climate change on water demand and supply is planned.

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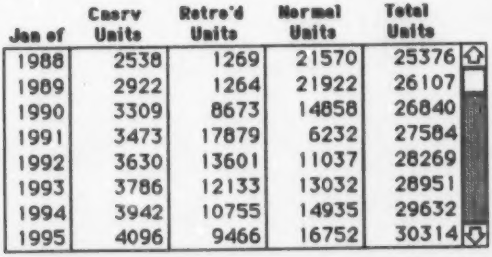
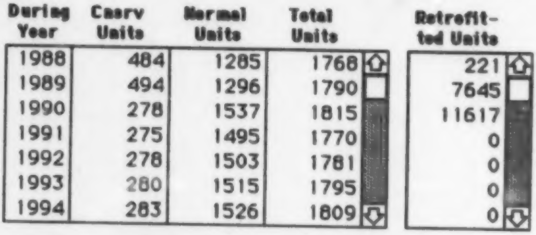
Figure 1. Output of a typical run of the Water Fixtures Module as it appears on the computer screen, giving the numbers of housing units by fixture class and by year.



Jan of	Cnsrv Units	Retro'd Units	Normal Units	Total Units
1988	2538	1269	21570	25376
1989	2922	1264	21922	26107
1990	3309	8673	14858	26840
1991	3473	17879	6232	27584
1992	3630	13601	11037	28269
1993	3786	12133	13032	28951
1994	3942	10755	14935	29632
1995	4096	9466	16752	30314

Figure 2. Output of the same run of the Water Fixtures Module as in Figure 1, giving the numbers of housing units requiring new fixtures and/or new retrofitting.



During Year	Cnsrv Units	Normal Units	Total Units	Retrofit-ted Units
1988	484	1285	1768	221
1989	494	1296	1790	7645
1990	278	1537	1815	11617
1991	275	1495	1770	0
1992	278	1503	1781	0
1993	280	1515	1795	0
1994	283	1526	1809	0

Figure 3. Program selection chart Selections are made by the computer operator by means of mouse clicks in the appropriate rectangles.

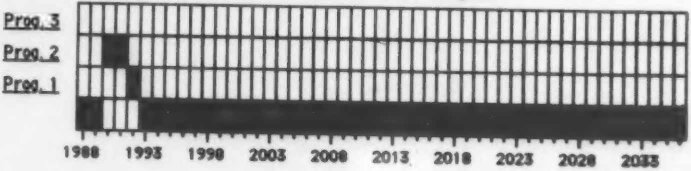


Table 1. Yearly calculations of the Water Fixtures Module. The example is the same as that of Figures 1 and 2. All numbers refer to housing units. 'Loss' refers to loss through normal wear and tear, which, in the case of fixtures, must be made up by 'replacement'. 'New units' refers to housing units built in the current year, while 'conversion' produces conserving units or retrofitted units from normal units.

		conserving	retrofitted	normal	total
1. starting		2,538	1,269	21,570	25,376
2. fixtures	a. loss	-100	-50	-846	-995
	b. replacement	+149		+846	+995
	c. new units	+292		+439	+731
	d. conversion	+42		-42	
3. retrofitting	a. loss		-177	+177	
	b. conversion		+221	-221	
4. final		2,922	1,264	21,922	26,107

Volume

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ENVIRONMENTAL RESEARCH

TECHNOLOGY TRANSFER CONFERENCE · CONGRES SUR LE TRANSFERT DES TECHNIQUES

LES RECHERCHES SUR L'ENVIRONNEMENT

ISSN 0825-4591

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FEATURE PRESENTATIONS
EMISSIONS AND EFFLUENTS
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TECHNOLOGIES/BIOTECHNOLOGY

THE MULTI-MEDIA APPROACH: Integrated Environmental Protection

November 25 & 26, 1991
Four Seasons
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Introduction

Environment Ontario holds its annual Technology Transfer Conference to report and publicize the progress made on Ministry-funded projects. These studies are carried out in Ontario Universities and by private research organizations and companies.

The papers presented at the Environmental Research: 1991 Technology Transfer Conference are published in two volumes of conference proceedings corresponding to the following sessions:

VOLUME I: FEATURE PRESENTATIONS
ENVIRONMENTAL TRANSPORT AND FATE
ENVIRONMENTAL EFFECTS
ENVIRONMENTAL MANAGEMENT OPTIONS

VOLUME II: FEATURE PRESENTATIONS
EMISSIONS AND EFFLUENTS
ENVIRONMENTAL TECHNOLOGIES PROGRAM
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Volume II is comprised of presentations given during Session D, Session E, Session F and Session G of the conference, as well as all Feature Presentations.

For reference purposes, indices for all sessions may be found at the front of both volumes.

For further information on any of the papers, please contact either the authors or the Research and Technology Branch at (416) 323-4649 or 323-4573

Acknowledgments

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Disclaimer

The views and ideas expressed in these papers are those of the authors and do not necessarily reflect the views and policies of Environment Ontario, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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Environmental Transport and Human Exposure: A Multimedia Approach in Health-Risk Policy

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Introduction

In his treatise *Air, Water, and Places*, the ancient-Greek physician Hippocrates demonstrated that the appearance of disease in human populations is influenced by the quality of air, water, and food; the topography of the land; and general living habits. This approach is still relevant and, indeed, the cornerstone of modern efforts to relate public health to environmental factors. What has changed is the precision with which we can measure and model these long-held relationships. Today, environmental scientists recognize that plants, animals, and humans encounter environmental contaminants via complex transfers through air, water, and food and use multimedia models to evaluate these transfers. In this talk, I explore the use of multimedia models both to examine pollution trends and as a basis for characterizing human health risks and ecological risks. The strengths and weaknesses of the approach are discussed.

I begin with a review of multimedia models—how they came about and where they are going. I highlight areas of success, areas of weakness, and areas that need much more work—such as plant-soil-air modelling. Next, I look at recent efforts to integrate multimedia models with exposure models to develop a more complete picture of human exposure to environmental contaminants. This is followed some ideas about the formal treatment of uncertainty in multimedia models and how this could bring about a better understanding of their precision and accuracy. Finally, I will discuss some new directions for multimedia model research.

Multimedia Models

Efforts to assess human exposure from multiple media are not particularly new. The need to assess human exposure to global fallout in the 1950's led rapidly to a framework that included transport both through and among air, soil, surface water, vegetation, and food chains. Efforts to apply such a framework to nonradioactive organic and inorganic toxic chemicals have been more recent and have not as yet achieved the level of sophistication extant in the radioecology field.

The first widely used multimedia compartment models for organic chemicals were the "fugacity" models developed by Mackay (1979, 1991) and Mackay and Paterson (1981, 1982). Cohen and Ryan (1985) introduced the concept of the multimedia compartment model as a screening tool with the MCM model. At the Lawrence Livermore National Laboratory (LLNL), we have developed a multimedia screening model, called GEOTOX (McKone and Layton, 1986), which was one of the earliest multimedia models to explicitly address human exposure for nonradioactive contaminants.

In a multimedia model we lump major components of the environment into homogeneous subsystems or compartments that can exchange mass with other adjacent compartments. Quantities, concentrations, or fugacities within compartments are described by a set of linear, coupled, first-order differential equations, which can be solved under steady-state or dynamic conditions. A compartment is described by its total mass, total volume, solid-phase mass, liquid-phase mass, and gas-phase mass. Mass flows among compartments include solid-phase flows, such as dust suspension or deposition, and liquid-phase flows, such as surface run-off and ground-water recharge. The transport of individual chemical species among compartments occurs by diffusion and advection at the compartment boundaries. Each chemical species is assumed to be in chemical equilibrium among the phases within a single compartment. However, there is no requirement for equilibrium between adjacent compartments. Decay and transformation processes (such as radioactive decay, photolysis, biodegradation, etc.) are treated as first-order, irreversible removals. The compartment structure we are using for assessing the regional impacts of toxic substances in air, water, and soil is illustrated in Figure 1.

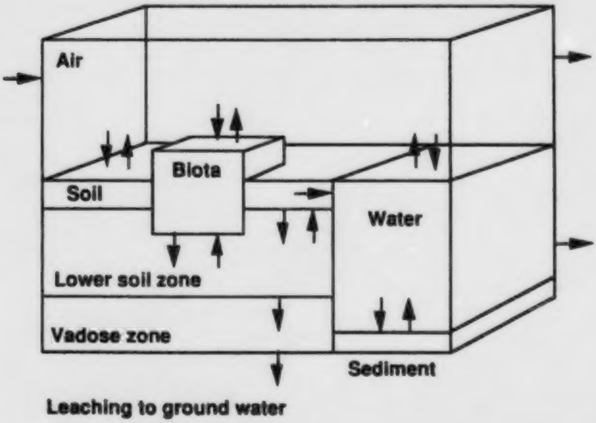

Figure 1. An illustration of mass exchange processes modeled in a seven-compartment environmental transport and transformation model.

Multiple Pathway Exposures

Human exposures to environmental contaminants result from contact with contaminated soils, water, air, and food as well as with drugs and consumer products. The extent of such exposures depends on (1) human factors and (2) the concentrations of a chemical in contact media. Human factors include all behavioral, sociological, and physiological characteristics of an individual that directly or indirectly affect his or her contact with the substances of concern. The principal output of an exposure assessment is a quantitative estimate of contact, expressed as mass of chemical per kg body weight per day. Exposures should be estimated for specific routes (i.e., inhalation, ingestion, and dermal uptake) because route-specific uptake, distribution, and metabolism are accounted for in pharmacokinetic models that could be used in risk assessments.

An early approach for systematically assessing multiple pathway exposures to nonradioactive environmental contaminants is the exposure commitment method (ECM) (Bennett, 1981). Exposure commitments (i.e., contaminant concentration in human tissue) are calculated from transfer factors that are the ratios of the steady-state concentrations of contaminants in the compartments of an exposure pathway. An exposure commitment is determined by multiplying the transfer factors of a given pathway, for example, air—>plants—>livestock—>diet. This method has been applied to organic chemicals and metals. Applications of the ECM are retrospective and depend on measured concentrations of the substances in the different compartments to estimate transfer factors.

McKone and Daniels (1991) have developed an approach that explicitly allows for the estimation of exposures to a substance based on either measured or predicted concentrations of the substance in contact media. Pathway-exposure factors (PEFs) are used to link chemical concentrations in multiple environmental media to human exposure by route—inhalation, ingestion, uptake. Specifically, each PEF numerically translates a chemical concentration in each of the primary environmental media (air, water, and soil) into exposure rates (in mg/kg-d) for each route of exposure. Incorporated into each PEF is information on human physiology and life style, as well as data describing pollutant behavior in food chains or in microenvironments, such as indoor air. In contrast to the ECM, this approach is prospective. This type of prospective approach has been used by Chetty (1991) to assess the impacts of benzene and pyrene in the Los Angeles basin.

Uncertainties

At best, mathematical models only approximate real systems, and therefore their predictions are inherently uncertain. The need to address human exposure in a multimedia framework brings with it a need to characterize the uncertainty in human exposure models and the combined uncertainty in exposure and dose/response models. In characterizing uncertainty in exposure models, three key issues should be considered: (1) uncertainty in predicting the relationship between sources of contaminants and concentrations in the accessible environment; (2) uncertainty in quantifying pathway-exposure factors (PEFs) that relate environmental concentrations to levels of exposure; and (3) the important contributions to the combined uncertainty in environmental dispersion and pathway-exposure factors.

Future Directions

In their efforts to construct new multimedia-exposure models, environmental scientists should recognize the importance of being both comprehensive and realistic in developing exposure scenarios. In addition to an emphasis on comprehensive human exposure modelling and formal treatment of uncertainties, there are four other areas that, I believe, will be important for the future of multimedia models—(1) formal validation studies (2) improved air-plant-soil models, (3) ecological risk assessment, and (4) ecological economics. Little real progress with multimedia models will occur until there is a coordinated effort to validate a multimedia model both with measured data and with other models. The recent literature reveals new understanding about the transfer of contaminants among soil, air, and terrestrial plants and this information needs to be incorporated into the next generation of multimedia models. Also, multimedia models could provide valuable input to the process of calculating ecological risk, but so far the literature in this area is incomplete. Finally, the newly established field of ecological economics (Costanza, 1989), which seeks to address broad-scale relationships between ecosystems and economic systems, is an area well-suited match to the multimedia approach, but the courtship has yet to begin,

Acknowledgements

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Dioxin Analysis State-of-the-Art:
the study of multimedia contaminants

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Introduction

Studies of the sources, transport and fate, and effects of the chlorinated dibenzo-p-dioxins (dioxins) and dibenzofurans (furans) are among the most difficult in environmental research. Central to these investigations are effective analytical methods that can quantify ultra-trace concentrations of dioxins/furans in a wide range of complex sample types. Developments in science as applied to toxic environmental contaminants essentially are the story of the dioxins/furans, as there is a close parallel between advances in analytical methods and advances in the environmental sciences. Because of the numerous studies of dioxins/furans in air, water, soil, industrial emissions, and in human and animal tissue, the dioxins and furans may be considered the first chemicals studied as true multimedia contaminants.

The History of Dioxin and Furan Contamination

Environmental contamination episodes. In 1957 millions of broiler chickens in the U.S.A. died after ingesting toxic compounds in feed fats. It was not until 1966 that one of the toxic compounds was identified as 1,2,3,7,8,9-hexachlorodibenzo-p-dioxin (1,2,3,7,8,9-H_6CDD) by x-ray crystallography. In the 1960's attention was focused on 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) produced as a trace side-product in the manufacture of chlorophenols. Since chlorophenols were used as starting products in the manufacture of a number of industrial chemicals including the widely used herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2,3,7,8-TCDD contamination of the environment became widespread. Incidents such as the spraying of Agent Orange in Vietnam from 1962-1970; the industrial accident at Seveso, Italy in July, 1976; and improper waste disposal at many Missouri sites during the early 1970's that resulted in the 1982 evacuation of the town of Times Beach, received intensive public scrutiny and are now well-documented. The presence of these chemicals in old chemical dump sites such as the Love Canal has also been highly publicized. In 1968 and 1979, cases of human poisoning from accidental ingestion of PCBs occurred in Japan and Taiwan, respectively. The presence of some chlorinated dibenzofurans in the PCBs was thought to be the principal agent responsible for the adverse health effects observed. Other studies showed that furans are formed during the uncontrolled burning of PCBs after a series of PCB-filled capacitor fires occurred in several different countries. One of the most publicized capacitor fires took place in an office building in Binghamton, N.Y. in 1981. Furans are also found in chlorophenols and related industrial chemicals. The above issues are all described in references 1-4.

Other sources of dioxins and furans. In 1977 dioxins were found in the fly ash from municipal waste incinerators in The Netherlands (5). The following year, this finding was confirmed in fly ash from Ontario incinerators (6). In 1979 the New York State Department of Health announced the finding of 2,3,7,8-TCDD in two Lake Ontario fish. The Ontario Ministry of the Environment (MOE) set up a special laboratory to study this issue in October, 1980. By 1981 a data base of a few hundred analyses of 2,3,7,8-TCDD in fish was developed separately by Ontario and by New York State. Since the finding of 2,3,7,8-TCDD in fish showed that some waterborne route of contamination existed, MOE also began testing Lake Ontario surface water and drinking water. MOE's detection limits were 10 parts per trillion (ppt) in fish and 1ppt in 1L water samples (7). In September, 1985, the U.S. EPA found elevated levels of 2,3,7,8-TCDD in a few fish sampled in areas near Pulp & Paper mills. Intensive investigations by MOE during 1985-86 confirmed that dioxins and furans were contaminants of mills that employed chlorine in the bleaching process (8). In 1989 the Ontario petroleum refining industry was found to be a source of dioxins and furans during the regeneration of spent catalyst material used in the catalytic reforming process (9). Other sources were characterized in the late 1980's. These included automobile exhaust (10), metal recovery facilities (11), steel mills (12), and other metallurgical industries (13).

Enough is now known to suspect any combustion process as being a possible source of dioxins and furans. This was stated a decade ago by the Dow Chemical Company as the "Trace Chemistries of Fire" hypothesis (14). Little work has been performed on natural combustion sources such as forest fires, but a recent MOE study has shown that dioxins and furans are formed under forest fire conditions (15).

Dioxins and Furans as Multimedia Contaminants

All of the above studies show that humans can be exposed to dioxins and furans from air, water, and soil exposure pathways. A recent investigation showed that food commodities accounted for up to 95% of the exposure of Ontario residents to these chemicals (16). However, this exposure only amounted to 23% of the total tolerable daily intake (TDI) of 2,3,7,8-TCDD (Toxicity Equivalents or TEQ, see below) of 10 picograms (pg) per kg body weight (kg bw). All routes of exposure must be included in any model used to estimate exposure of humans to dioxins and furans. The multimedia exposure model used for Ontario has been described (17).

The basis for the multimedia approach is straightforward: once the maximum exposure level for a chemical has been determined, this quantity must be apportioned between all routes of exposure to protect human health. In this way, the combined exposure permitted by the separate guidelines would not exceed the TDI. Since food is the principal exposure pathway for Ontario residents, most of the tolerable daily dose would be apportioned to this pathway when determining guidelines. The net effect of the dose allocation exercise is that the guidelines set for any one exposure pathway will be much lower than if the entire daily tolerable dose was considered. The multimedia approach thus provides an effective means to protect human health, and in a sense symbolizes the interconnectedness of the ecosystem. The scientific advances in multimedia standard setting for the dioxins/furans can be applied to other environmental contaminants.

Challenges in the Analysis of Dioxins

The need for low detection limits. There are several reasons why parts-per-trillion (ppt) and parts-per-quadrillion (ppq) detection limits are required:

- ❑ the LD_{50} for 2,3,7,8-TCDD is about 1.0 μg/kg bw in the most sensitive species
- ❑ dioxins are hydrophobic and lipophilic, and consequently have high bioconcentration factors - therefore low detection limits are required to identify and track sources, especially in aquatic systems
- ❑ for the study of dioxin levels in human and animal tissues, sample sizes may be very small
- ❑ long-term chronic effects from low-level exposures are not well understood

The need to separate dioxins from other organics in the sample. This task is the most challenging and the success with which sample cleanup is performed will determine the detection limits, precision, and accuracy that are attained. Since dioxins may be present in the final sample extract at low picogram quantities, they may be "swamped out" by other organics that are present in quantities thousands of times greater. The sophisticated gas chromatograph-mass spectrometer (GC-MS) systems employed for the final separation and detection steps of the analysis, although highly selective, cannot achieve ppt and ppq detection limits unless presented with a "clean" sample in which virtually all other organics have been removed. It should also be remembered that highly contaminated samples where dioxin levels may be significant are precisely those samples where other chlorinated organic compounds - structurally similar to the dioxins and therefore potential interferences - are also likely to be present.

The need to separate the dioxins from each other. Of the 210 possible chlorinated dioxin/furan structures, only 17 are thought to be of toxicological significance. These are the ones with chlorine substitution at the 2,3,7 and 8-positions of the basic structure. The other "non-toxic" dioxins and furans are therefore interferences for the 17 "toxic" compounds. Schemes have been developed to relate the relative toxicity of each 2,3,7,8-substituted dioxin/furan with that of the most toxic: 2,3,7,8-TCDD. For example, octachlorodibenzo-p-dioxin (OCDD) is considered to be 1000 times less toxic than 2,3,7,8-TCDD, while 2,3,4,7,8-pentachlorodibenzofuran (2,3,4,7,8-P_5CDF) is thought to be one-half as toxic. Therefore "toxicity equivalent", or TEQ factors can be applied to the concentrations of OCDD and 2,3,4,7,8-P_5CDF in a sample to determine their "2,3,7,8-TCDD-toxicity equivalent" concentrations. The OCDD concentration is multiplied by 0.001, while the 2,3,4,7,8-P_5CDF concentration is multiplied by 0.5. By doing this for all 17 of the 2,3,7,8-substituted dioxins/furans and then summing up the "2,3,7,8-TCDD-toxicity equivalent" concentrations, a total TEQ value is obtained that is very useful for regulatory and risk-assessment activities. However, this exercise is only effective if the "toxic" and "non-toxic" dioxins/furans can be separated from each other. Since the 210 dioxins/furans are so similar in structure to each other, this is not an easy task.

Dioxin Analysis State-of-the-Art

The challenges described above, although substantial, have largely been solved. High resolution GC-MS systems are available that can routinely detect 100 femtograms or less of 2,3,7,8-TCDD. Detection of 10 fg has been reported. Complex cleanup schemes have been developed that effectively isolate the dioxins/furans from potential chemical interferences in the most difficult sample types. The keys to successful cleanup are the number of separation steps employed, and the care and skill provided by the analyst. By using a series of gas chromatographic columns, and/or a combination of gas chromatography and high performance liquid chromatography, definitive separation of all 2,3,7,8-substituted dioxins and furans from all non-toxic dioxins/furans is possible.

Detection limits in real samples of ppt or better have been reported in samples of biota (including food) and soils; parts-per-quadrillion levels are routinely attained in 1L water samples; and detection of 0.01 pg/m^3 dioxin in ambient air is commonplace for the best 10-20 laboratories world-wide. A precision of 20-30% relative standard deviation (%RSD) for such work is possible if conditions and calibration standards are carefully controlled. However, it is not unusual to observe RSDs of 50-100% for dioxin in difficult samples when measurements are made near the method detection limit.

Where Do We Go From Here?

In a recent NATO survey, over 100 laboratories world-wide were identified that have some level of dioxin capability. Just 15 years ago, only about a dozen could make this claim. Of course, not all of these laboratories have the same level of expertise. There are probably no more than 20 labs who can boast state-of-the-art capability for isomer-specific determination of the 17 toxic dioxins/furans in virtually any matrix at ppt to ppq concentrations. One thing that even the top labs have not been able to do is to reduce the cost of analysis. It is still such a specialized area requiring highly trained staff and sophisticated, expensive instrumentation that private labs charge from $1,000 to $2,000 per analysis. Reduced cost for dioxin determinations would allow many more determinations to be performed. This would not only benefit environmental surveys (more locations monitored) and quality control (more replicates and round-robins), but would help multimedia investigations that are very sample-intensive (because all exposure pathways must be investigated).

Some researchers feel that some PCBs exhibit sufficient toxicity that they should be included with the 17 toxic dioxins/furans for the calculation of total TEQs. To do this would require even lower detection limits for the dioxins and furans. Since PCBs in sufficient concentrations are serious interferences for dioxin determinations, including some of them in the TEQ calculation would present a difficult challenge.

In the past 20 years, our knowledge of the formation, transport and fate, effects, and remediation of toxic environmental contaminants have greatly advanced because of dioxin/furan research. These advances would not have been possible without the parallel development of sophisticated analytical methodologies.

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C5

THE MULTIMEDIA APPROACH AND POLLUTION PREVENTION: WHAT DO WE KNOW? WHAT DO WE NEED TO KNOW?

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ABSTRACT

The theme of this conference is "The Multi-media Approach: Integrated Environmental Protection" and the theme of this session is "Environmental Management Options". This paper places these themes in the broader context of the economic literature, to reviews the implications of that literature for the conference themes, and considers directions for future economic research. Special emphasis will be placed on the potential role of experimental economics in evaluating environmental policy.

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THE MULTIMEDIA APPROACH AND POLLUTION PREVENTION: WHAT DO WE KNOW? WHAT DO WE NEED TO KNOW?

OUTLINE

This paper places the concept of Integrated Environmental Protection into the economic literature, reviews the implications of that literature for the environmental management, and considers directions for future economic research. Special emphasis will be placed on the potential role of experimental economics in evaluating environmental policy.

I Introduction

The theme of this conference is "The Multi-media Approach: Integrated Environmental Protection" and the theme of this session is "Environmental Management Options". This paper is intended to place these themes in the broader context of the economic literature, to review the implications of that literature for the conference themes, and to consider directions for future economic research. Special emphasis will be placed on the potential role of experimental economics in evaluating environmental policy.

It will be useful to define our terms. Environmental Management Options are institutions governing the interaction between the economy and the environment. On the one hand we can attempt to prescribe the exact conditions and quantities in which industrial, municipal and domestic wastes can be discharged to the natural environment. This is the "command-and-control" option often denounced in the economic literature. On the other hand we can attempt to manipulate the information people have and the incentives they face so as to encourage them to change their interactions with the natural environment. This is the so called "incentive based" option frequently advocated in the economics literature. Of course we could attempt some mixture of these somewhat opposing approaches. I shall have a considerable amount to say about this choice in the middle section of this paper.

The terms "multi-media approach", "integrated environmental protection", and "pollution prevention" are somewhat vaguer. In practice, it seems we are using a multi-media approach if we recognize that any waste discharged to any one medium (for example toxic wastes discharged to the air during incineration) may eventually wind up in a second medium (water, for example) and possibly reincorporated into human activity through even a third medium, such as the fish we eat. We are not using a multi-media approach if we speak about air, water, or soil pollution by itself. Thus calling for a multi-media approach to environmental protection is effectively a claim that exclusive focus on any one of air, land or water is going to lead to important errors in public policy.

"Integrated environmental protection", it would appear to me, has essentially the same content. I take it that our environment is protected in an integrated manner if we simultaneously control discharges to air, water and land. "Pollution Prevention", on the other hand, seems to refer more to the choice between "end-of-pipe treatment" of residuals and process innovations designed to reduce residual discharges.

II Multi-media Approaches in the Context of the Economic Literature

Stressing integrated environmental protection is consistent with a large body of literature in environmental economics. Two strands in the literature seem particularly relevant. These are the materials balance approach to environmental economics and the rapidly expanding literature on economics of sustainable development.

A The Materials Balance Approach

The materials balance approach dates back to Kneese and forms the introductory portion of all environmental texts. The relationship between the economy and the natural environment can be pictured in various ways. The natural environment contributed physical materials and intangible services to the human economy. The economy discharges wastes to the natural environment where they may affect the original flow of materials and services. All materials extracted from the environment are ultimately returned to it as residuals. Focus on this fact immediately leads to the problem of multi-media contamination, since the control of discharges to any one medium must necessarily alter discharges to another.

Recycling and pollution prevention can reduce the residual load placed on the environment, but they have labour, capital and natural resource requirements themselves. We must select the appropriate level of recycling and pollution prevention, while recognizing that reduced demands on the environment may have an opportunity cost is terms of reduced incomes and consumption of other goods.

B The Economics of Sustainable Development

There is a large and growing literature on the economics of sustainable development. Much progress has been made in giving economic content to the idea of sustainable development. Here I wish to argue that efficiency should be a central concern of environmental quality management, and that it is too often neglected. In discussing policies for sustainable development, the literature also makes useful distinctions among general policies with environmental effects, framework policies concerning the environment, and issues surrounding project evaluation.

1 Sustainable Development and Efficiency

The literature distinguishes development from economic growth. Economic growth involves increases in measured income such as GNP. Development refers to indicators of human welfare. It is argued that growth cannot be sustainable, but that development can.

2 Policies for Sustainable Development

Stimulating work on environmental policy has occurred at all three levels. At the level of general policies, new developments in National Accounting are leading to the incorporation of depreciation of the Natural environment into the national accounts. At the level of environmental policy, the great debate concerns the choice between command-and-control regulation and incentive based regulation. Discussion of this is postponed to the next section. At the level of project evaluation, sensible suggestions have been made for the incorporation of environmental concerns, but general practice in the field lags far behind.

III The Choice of Regulatory Regime

This section focuses on the choice between Command and Control and incentive based regulation. The paradox is the great enthusiasm evidenced for market based schemes in the Green Plan and elsewhere while the assessments of the US market based schemes are surprisingly pessimistic. Several explanations for the limited success of these schemes are examined.

We may react to the presence of environmental problems in several ways: we may ignore them, we may try to solve them through the private law system, or we may try to regulate. In the last case we are faced with the choice between command and control and incentive based regulation. The case for incentive based regulation seems strong: incentive based regulations should minimize the cost of attaining any given level of environmental control and should provide strong incentives for the development of new control technologies. But the experience in the United States, especially with air emissions trading, has been only a modest success. Far fewer trades are made than had been expected. Explanations offered include excessive restrictions on trades (levels, sequential trades, the need to meet standards at every point (see Merrivell, Atkinson and Tietenberg), and political difficulties in getting the concept accepted. This last literature suggests concerns about the income distributional consequences of emission trading schemes is important.

IV The Contribution of Experimental Economics

This section suggests that some of the difficulties encountered in promoting and testing the ideas of incentive based regulation can be answered by laboratory experiments. Economics is not usually considered to be an experimental science. There is a growing literature, however, that tests the effectiveness of economic institutions in a laboratory setting. The systematic examination of institutions for allocating environmental rights is only beginning. There are, however, a number of experiments that show great promise. Further work in this area is advocated.

V Conclusion

This paper has attempted to place the themes of environmental management options and the multi-media approach to pollution prevention into the context of the economic literature. It has argued that great progress has been made in suggestions for incorporating environmental concerns into economic decisions, but that practice lies well behind theory. The debate between command-and-control and incentive-based regulation is unresolved. The newly developing field of experimental economics shows substantial promise in helping us to understand the nature of the debate.

D3 Costs and Benefits of Improved Environmental Control - Some Case Histories at INCO; W.C. Ferguson, INCO Limited, Toronto, Ontario

PAPER NOT AVAILABLE AT TIME OF PRINT

F2 A Consumer Perspective to Waste Prevention and Reduction; R. Lotzkar, Environmentally Sound Packaging Coalition and Consumers' Association of Canada, Vancouver, British Columbia

PAPER NOT AVAILABLE AT TIME OF PRINT

G7 Close Encounters of the Immune Kind: Antibody-Based Tests for Environmental Chemicals; B. Ferguson, ImmunoSystems Inc., Scarborough, Maine, U.S.A.

PAPER NOT AVAILABLE AT TIME OF PRINT

VOLUME II

SESSION D

EMISSIONS AND EFFLUENTS

VERBAL PRESENTATIONS

Modelling the influence of topography
on dense gas dispersion II: Algorithm development

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1 INTRODUCTION

Topography, in the form of general slope, isolated hills, or more complex terrain, will alter or divert a dense gas cloud or plume. The topography may enhance plume dilution and divert the plume away from regions of elevated terrain; or, the dense plume may be channelled into valleys or low-lying areas and then be protected from the diluting influence of the ambient flow. These important effects are not included in the models currently used to predict the dispersion of a dense gas cloud for risk assessment or emergency management.

The overall objective of the study is the development of methods for incorporating the effects of topography in numerical models of dense gas dispersion. Phase I of the project, reported previously, consists of an extensive review of the existing theory and experimental results applicable to the problem. Phase II of the project consists of the development of algorithms for incorporating the effect of topography into integral (box) models of dense gas dispersion. This paper outlines the development of algorithms, based on the previous review (Ramsay & Britter 1990a, 1990b, 1991a).

2 ALGORITHM DEVELOPMENT

Previous publications from this project (Ramsay & Britter 1990a, 1990b, 1991a) have shown that it should be possible to incorporate the effects of topography on dense gas dispersion within the box model formulation. These results have shown that these effects can be represented principally by: a modified advection velocity; and, a modified entrainment relationship. The treatment of other subsidiary aspects of the problem which are also necessary to provide a practical implementation of these ideas is outlined.

2.1 Relevance of slope

It is important to determine whether terrain effects should be considered or not. Fay & Ranck (1983) suggest a criterion, for an isolated release, that there will be no slope effect if

$$u_*^2 > \frac{g'_0 Q_0}{\pi R^2}\sin\theta \qquad (1)$$

this may be re-written as

$$\frac{g'_s \bar{z}}{u_*^2} < \frac{1}{\sin\theta} \qquad (2)$$

where θ is the slope. This appears to be a reasonable criterion and might also be applicable to continuous plume releases.

2.2 Advection Velocity

It is shown in Ramsay & Britter (1990a, 1991c) that the advection velocity of the cloud is modified by topography.

There are two possible approaches to a modified advection velocity relationships in the model: a momentum equation approach; and, a modified advection velocity approach. Each of these approaches is discussed in the following sections.

2.2.1 Momentum Equation Approach

One possible approach for incorporating the effect of topography is to develop a momentum equation for a puff or plume. However, it is considered that this would obscure important aspects of the development and interpretation of the resulting model.

2.2.2 Modified Advection Equation Approach

Analysis and experimental results indicate that the advection velocity (for a plume) could be modelled as

$$U_a = U_{ambient} + U_d = U_{ambient} + C(g_e\bar{z})^{1/2} \tag{3}$$

where C is a function of the slope and the last term is the downslope velocity. The coefficient C is a weak function of slope and may be obtained from experimental results in the absence of any ambient wind. In these cases the flow adopts a constant value of

$$C = \frac{U_d}{(g_e\bar{z})^{1/2}} \tag{4}$$

due to a local balance between a downslope force and retardation due to skin friction and/or entrainment. The downslope velocity U_d is given by

$$\frac{g_e\bar{z}}{U_d^2}\cos\theta = \frac{E + C_D}{S_2\tan\theta - \frac{1}{2}ES_1} \tag{5}$$

where

$$S_1 = 0.25 \qquad S_2 = 0.75 \tag{6}$$

Solution of this equation requires and expression for the entrainment E. We shall use

$$E = 1.2\times10^{-3}\theta \tag{7}$$

for continuous or time-varying releases and the same expression with the coefficient 4.0×10^{-3} for instantaneous releases. These entrainment expressions are known to be valid for large (say $\theta > 5°$) slopes and have been used for slopes down to 6×10^{-3} degrees. At small slopes the use of

$$E = \frac{u_t}{U_a} = C_1\left(\frac{g_e\bar{z}}{U_a^2}\cos\theta\right)C_D^{3/2} \tag{8}$$

brings in the explicit dependence of entrainment on surface roughness.

Thus we must solve three equations to determine the entrainment E, the downslope velocity U_d and the advection velocity U_a.

We shall use the larger of the estimates of E based on θ and the estimate of E based on C_D. We shall use this result in continuous, time-varying and instantaneous releases. Note that this produces a reduced uphill advection velocity and an increased downhill advection velocity.

2.3 Modified Entrainment Equation

In dealing with entrainment we note two effects:

(i) Entrainment due to the difference between the buoyant downslope motion and the ambient motion. This difference is just $C(g' z)^{1/2}$. We appeal here to the basic entrainment relation from Ellison & Turner (1960) and others that an additional entrainment velocity

$$u_t = (U_a - U_{ambient})\,(1.2\times10^{-3}\theta) \qquad (9)$$

where θ is the slope in degrees which leads to

$$u_t = C(g_x\bar{z})^{1/2}\,(1.2\times10^{-3}\theta) \qquad (10)$$

should be included for plumes and the same expression with the coefficient 4.0x10-3

$$u_t = C(g_x\bar{z})^{1/2}\,(4.0\times10^{-3}\theta) \qquad (11)$$

(ii) A change in the surface generated turbulence. This might be expected to depend on the advection velocity. The proposal here is to model this using previous entrainment expressions but with u_* modified to

$$u_*\frac{U_a}{U_{ambient}} \qquad (12)$$

This is consistent with the small slope expression given above.

The correlation based on slope alone, i.e. (i), has, effectively, included (ii) albeit in an approximate way. Consequently we proceed in a manner consistent with the previous analysis and select the larger of the two estimates.

2.4 Reversing Flows

It is possible that the combined effect of topography and ambient wind will lead to a situation in which the motion of the cloud reverses. This situation is considered below for instantaneous and continuous releases.

2.4.1 Instantaneous Releases

These could move downslope and then upslope and this would be handled directly by the previous algorithms.

2.4.2 Continuous Release

This case could be handled directly to allow for the revening of the plume.However, we note that after the plume had reversed it would be interacting with the downslope plume. However, the downslope extent is limited by plume widening rather than by dilution. Consequently, the model would determine the width at the maximum downslope extent and then consider an undiluted, wide plume starting from this position.

2.5 Ambient Wind

When the ambient wind is not normal to the slope the model will consider the downslope velocity

$$C(g_e\overline{z})^{1/2} \qquad (13)$$

in two components parallel and normal to the wind direction. The along wind component is used as before while the across wind component provides a normal velocity, the respective magnitudes providing the plume/puff direction.Entrainment would be treated as previously in two parts: and increased surface generated turbulence and an explicit slope dependent part.

2.6 Wind field determination

The topography will alter the wind field substantially. Three approaches are possible for estimating the altered wind field:

i) Estimation of the maximum and minimum changes from analysis and experiment (e.g. Britter, Hunt & Richards 1984 and others) followed by interpolation. For example, Britter (1982) estimated that for flow over a hill of height h and length L (the half length to the half height, is about 25% of the overall length of the hill) there will be an increase in the local friction velocity u. by

$$u_* \frac{h}{L}\left(\frac{U(L)}{U(\xi)}\right)^2 \qquad (14)$$

where U(z) is the incident ambient velocity profile and

$$\frac{l}{L}\ln\left(\frac{\xi}{z_0}\right)=2\kappa^2 \qquad (15)$$

where κ.

The decrease in u. at the hill base will be similar. The velocity profile may be determined from the modified u., z_0, L, H and ξ. More sophisticated estimates are possible.

ii) Use specific codes (e.g. MS3DJH, FLOWSTAR or MSFD) for wind fields in complex terrain.

iii) Specific codes might be used for a number of standard cases e.g. plateau to slope, plateau to slope to plateau etc., and a simple library formulated.

We will initially use the first approach.

3 RESULTS

Preliminary results have been obtained using these algorithms in the GASTAR dense gas dispersion model (Ramsay 1990). Figure 1 shows results for an instantaneous release similar to the Thorney Island trial 15 with no slope, and for upslope and down slope winds on a 5° slope. The radius and the concentrations are plotted as functions of the location of the cloud centroid. The upslope wind increased the radius of the cloud relative to the no slope case and the downslope wind decreased the radius. The concentration was increased relative to the no slope case for a downslope wind and decreased for an upslope wind. Figure 2 shows the results for a release similar to a Thorney Island test on a slope of 10° with the wind at 45° to the slope.

4 CONCLUSIONS

The results of the first two phases of this project have clearly indicated that the dominant effects of topography can be incorporated within the box model formulation of dense gad dispersion. The approach used involves a modified advection velocity and a modified entrainment relationship, together with subsidiary conditions required to provide a practical implementation of these ideas.

Preliminary results have shown good agreement between box model predictions using the GASTAR denes gas dispersion model and experimental results. The two remaining phases of this project will further explore the implementation of these algorithms in a dense gas dispersion model, for routine risk assessment and emergency management use and comparison tests with experimental data and more sophisticated model results.

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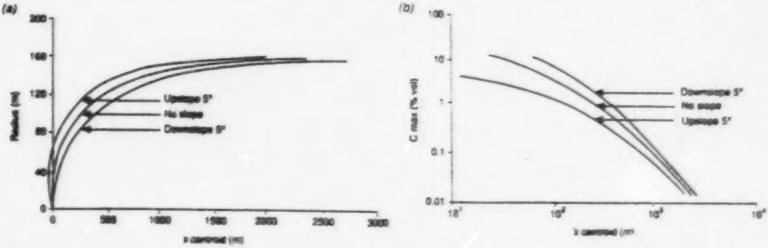

FIGURE 1 The effect of slope on Thorney Island trial 15 instantaneous release results. (a) radius (b) centreline concentration.

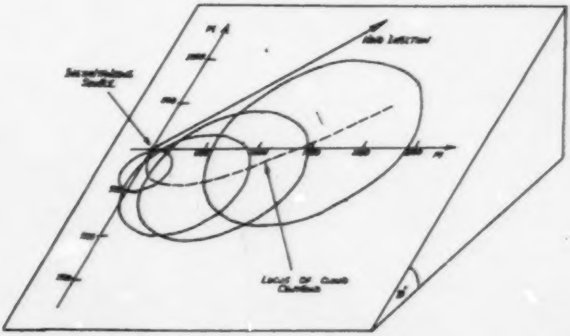

FIGURE 2 Effect of slope on an instantaneous release similar to the Thorney Island releases on a 10^0 slope with ambient wind at 45° to the slope. The cloud initially moves down the slope under the influence of the negative buoyancy, then dilutes and is driven up the slope by the ambient wind.

D2

PRACTICAL APPLICATION OF FECAL COLIFORM (FC) TO STREPTOCOCCUS FAECIUM SUBSP. CASSELIFLAVUS (SC) AND BIFIDOBACTERIUM TO SC RATIOS TO DETERMINE HUMAN AND ANIMAL SOURCES OF POLLUTION.

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INTRODUCTION

Fecal coliforms and *Escherichia coli* (EC) are routinely used as fecal pollution indicators. However, these organisms are found in both human and animal feces and therefore cannot be used as indicators of strictly human input. Many organisms pathogenic to humans are also found in animals; one example is *Campylobacter jejuni* (Manninen *et al*., 1982). Other pathogens, such as the hepatitis A virus (Shinhoj, *et al*. 1980), are human-specific. Since these organisms can be transmitted via the fecal-oral route, it is important to be able to assess whether the pollution comes from a human or animal source.

Streptococcus faecium subsp. *casseliflavus* (SC) has been shown in earlier work to be present in animal but not in human fecal samples (Seyfried *et al*., 1990). Studies are currently underway to examine the feasibility of utilizing this organism in an EC:SC ratio model to predict the origin of fecal pollution.

Mossel proposed the use of bifidobacteria as indicators of fecal contamination in 1958 (D.A.A. Mossel, Abstr. 7th Int. Congr. Microbiol., 1958, p. 440); however, more work is necessary to determine their true potential. In principle, *Bifidobacterium* spp. have all the characteristics of an ideal indicator. For example, they are found in high densities in fecal material (Mitsuoka and Kaneuchi, 1977); they are incapable of surviving in the oxygenated extraenteral environment and therefore show promise as an indicator of recent fecal contamination (Oragui, 1982); and the possibility of developing a reliable test to determine human or animal sources of pollution exists (Cabelli, 1979; Resnick and Levin, 1981).

Our previous studies have shown that Bifidobacterium spp. and S. faecium subsp. casseliflavus can be recovered from sanitary and storm sewers (Seyfried et al. 1990). Methods are being developed to facilitate the isolation and characterization of these organisms and to study their rates of survival. This paper reports on a study assessing the use of these organisms to determine the impact of wildlife and other types of fecal pollution on the Kelso Conservation area.

METHODS

Sampling sites

The nine sampling sites were located on Sixteen Mile Creek in the Kelso Conservation area and in the City of Milton.

Sample collection

Surface water samples were collected in sterile bottles on a weekly basis. The samples were collected between 9:00 a.m. and 12:00 noon because our earlier studies showed that incident radiation between noon and 3:00 p.m. on sunny days caused a drop in bacterial levels (Seyfried, 1973). Processing in the lab was within 5h of collection.

Human and animal fecal specimens were also collected for analysis.

Isolation and characterization methods

Escherichia coli

Samples were filtered through 0.45 - µm (pore size), 47 - mm - diameter type GN-6 membrane filters (Gelman Sciences, Ann Arbor, Michigan). The filters were placed on mTEC medium and incubated in plastic containers with bottles of ice at 44.5°C for 24 h. To test for urease production, the filters were transferred to petri dishes containing pads saturated with urea. All yellow colonies were counted, after a 15 min incubation, as presumptive *E. coli*.

Streptococcus faecium subsp. *casseliflavus*

The isolation medium consisted of the m-Enterococcus agar (Difco) formulation without the addition of 2,3,5 - triphenyl tetrazolium chloride. Samples were membrane filtered and the filters were placed on the agar surface. Incubation was at 37°C for 48 h. The colonies appeared pale, lemon, or bright yellow in colour. For confirmation, filters were placed on plates of nutrient agar with 2% gelatin. Following incubation at 37°C for 1.5 h, the filters were removed and the plates were flooded with mercuric chloride solution (Mates, 1983). The target colonies are gelatinase negative as well as xylose and raffinose positive. Arginine hydrolysis and pyruvate tests were carried out on selected isolates.

Bifidobacterium spp.

The isolation medium employed was Lactobacillus - MRS (Difco) with 0.03% cysteine hydrochloride added. Appropriate dilutions of each sample were spread plated onto the agar surface. Plates were incubated at 37°C for 48 h in anaerobic jars containing an anaerobic gas pack (BBL 70304) and an indicator strip (BBL 70504). Typical bifido colonies appeared procelain white (pearl-like), opaque, mucoid, concave, round, and entire.

Additional methods used to further classify and speciate the bacteria included the F6PPK (fructose-6-phosphate phosphoketolase) test (Scardovi, 1986) and the API Rapid CH test (API Laboratory Products Ltd., St. Laurent, Quebec).

Survival studies

E. coli C3000 was grown for 24h at 37°C in nutrient broth. A 1mL aliquot was added to 9 mL phosphate-buffer solution and this diluted culture was then placed in a flask with 90 mL of filter-sterilised farm pond water. Incubation of each flask was at 0°C, room temperature, or 37°C. *S. faecium* subsp. *casseliflavus* was grown for 24 h at 37°C in Brain Heart Infusion broth (Difco) and diluted into pond water as described for *E. coli*. Samples were taken weekly and plated onto the selective medium noted previously for each organism.

RESULTS AND DISCUSSION

The analysis of human and animal fecal specimens showed that, in humans, *E. coli* (EC) densities averaged 4.03 x 10^6 per gram. To date, no *S. faecium* subsp. *casseliflavus* (SC) has been isolated from human feces; therefore, the calculated EC:SC ratio for human feces would be 4.03 x 10^6. In comparison, analysis of over 30 horse fecal specimens yielded an average of 6.46 x 10^4 *E. coli* per gram and 6.23 x 10^4 *S. faecium* subsp. *casseliflavus* per gram. Thus the ratio of EC:SC for horses is close to 1.0. Other animals studied also had approximately equal densities of EC and SC.

Preliminary field studies were conducted in the Kelso Conservation Area to assess the feasibility of using the EC:SC ratio as a means of determining whether pollution input is of human or animal origin.

The data obtained from HFI and M2, two of the nine sampling sites shown in Fig. 1, are presented here for comparative purposes. The HFI location has animal input from wildlife. Racoon and deer feces collected from the area had *S. faecium* subsp. *casseliflavus* levels ranging from 1.0 x 10^5 to 3.8 x 10^6 CFU per gram. *Escherichia coli* densities in the fecal specimens ranged from 1.7 x 10^5 to 1.4 x 10^8. The M2 site is representative of human pollution input because of outflow from the Milton sewage treatment plant.

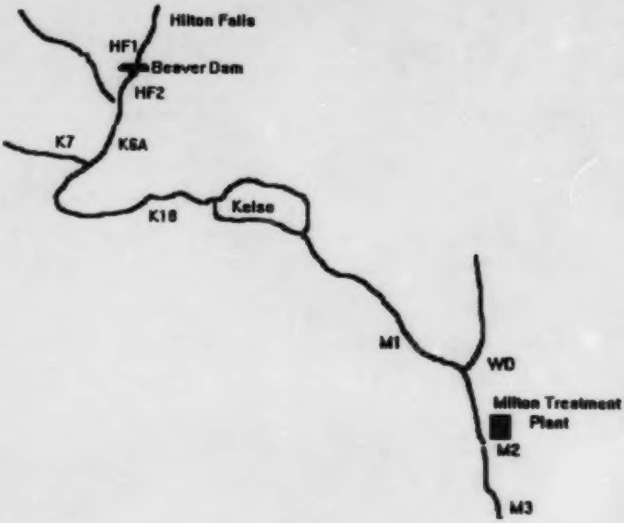
Hilton Falls
HF1
Beaver Dam
HF2
K7
K6A
K18
Kelso
M1
WD
Milton Treatment Plant
M2
M3

FIG. 1. Sampling locations on Sixteen Mile Creek.

Table 1. Comparison of *E. coli* (EC) and *S. faecium* subsp. *casseliflavus* (SC) levels and ratios at the HFI site, which has animal impact, and at the M2 sewage treatment plant location.

Date (1991)	Sampling Site HFI EC	:	SC[a]	M2 EC	:	SC
June 25	141	:	11 (12.8)		ND	
July 2	122	:	29 (4.2)	11	:	0 (11)
July 9		ND		39	:	0 (39)
July 16	400	:	24 (16.7)	96	:	0 (96)
July 23		ND		23	:	0 (23)
July 30	1000	:	101 (9.9)	2400	:	0 (2400)
Aug. 6		ND		198	:	0 (198)
Aug. 13	185	:	20 (9.3)	80	:	10 (8)
Aug. 20		ND		20	:	0 (20)

[a] CFU/100 mL of *E. coli* and *S. casseliflavus*

( ) = Calculated ratio

ND = Not determined

As may be seen from Table 1, apart from one sample collected on August 13, no *S. faecium* subsp. *casseliflavus* organisms were isolated from samples collected at the main outflow pipe of the Milton sewage treatment plant. This resulted in an average EC:SC ratio of 349.4 at this site which had a major human pollution input. The average EC:SC ratio of samples taken from the HFI site, where there was a wild animal pollution source, was 10.6. Although the detailed results are not presented here, the EC:SC ratios determined for the other sampling sites approximated those found at the HFI location. These seven sites received input from farm runoff and other animal sources.

A more precise assessment of the type of animal pollution input would be helpful in tracing, for example, runoff from different point sources. To determine if it is possible to identify an individual animal source, S. faecium subsp. casseliflavus isolates from a variety of animal fecal specimens were examined for their colony morphology and biochemical characteristics. Some differences between animals were noted. For example, the pigment and colony texture varied from a soft, lemon yellow colony for sheep to a bright yellow, dry and sticky colony for pigeons. Differences were also noted in the arginine hydrolysis and pyruvate reactions as shown in Table 2.

Table 2. Arginine hydrolysis and pyruvate reactions in S. faecium subsp. casseliflavus isolates from various animal sources.

Animal Source	Number of isolates	Arginine hydrolysis	Pyruvate
Horse	85	+ (100%)	– (96.5%)
Pigeon	7	+ (100%)	+ (57.1%)
Chicken	24	+ (100%)	– (100%)
Goat	6	+ (100%)	– (100%)
Goose (domestic)	18	+ (94.4%)	± (94.4%)
Goose (wild)	13	+ (100%)	– (100%)
Pig	1	+ (100%)	– (100%)
Turkey	2	+ (100%)	± (50%) – (50%)
Cow	7	+ (85.7%)	– (100%)
Camel	1	+ (100%)	– (100%)
Chipmunk	1	+ (100%)	– (100%)
Sheep	40	+ (60.0%)	– (97.5%)

As may be seen in the Table, the arginine hydrolysis reaction was positive in almost all cases. Some variation was observed for the pyruvate reaction and this will be investigated further.

Mundt (1961) reported on the frequent recovery of enterococci from plants. Sherman (1937) also suggested that these organisms occur commonly on plants. In this study, samples of grass, hay, carrots and lettuce were analyzed and it was found that *S. faecium* subsp. *casseliflavus* densities on these plants were in the 2.0×10^1 to 1.56×10^4 CFU per gram range. When the EC:SC ratios were calculated they ranged between 0.005 and 0.05. Although these organisms are readily isolated from plants, Mundt concluded that they are only temporary residents, disseminated by the action of wind and insects. Since the plant EC:SC ratios appear to be very low, their interference in pollution source determinations will be minimal.

The results of the survival studies carried out in farm pond water are presented in Table 3.

Table 3. Percent survival of *E. coli* and *S. faecium* subsp. *casseliflavus* in pond water at varying temperatures over a two month period.

Organism	Number of weeks	0°C	Room Temperature	37°C
E. coli	2	99.10%	180.55%	7.69%
	4	7.50%	111.11%	0.06%
	8	2.10%	0.14%	0.01%
S. faecium subsp. *casseliflavus*	2	94.25%	28.89%	48.12%
	4	83.91%	7.33%	9.37%
	8	44.83%	0.60%	0.68%

The data showed that *E. coli* died off more rapidly at 0°C and 37°C than did *S. faecium* subsp. *casseliflavus*. However, at room temperatures ranging from 20 to 25°C there was regrowth of *E. coli*. Other researchers (Bonde, 1977, Evison and James, 1973) have shown that E. coli may be able to survive and regrow for extended periods in tropical habitats. Carrillo and coworkers (1985), for example, found that E. coli was able to regrow in the Mameyes River when the water temperature was 21 to 22°C. Although S. faecium subsp. casseliflavus survived longer than E. coli at temperatures of 0°C and 37°C, the regrowth phenomenon was not observed.

Table 4. Levels of Bifidobacterium spp. and E. coli per gram of human and animal feces.

Source	CFU per gram	
	Bifidobacterium spp.	E. coli
Human	6.31×10^7	4.03×10^6
Chicken	1.28×10^8	7.09×10^7
Horse	1.56×10^5	6.46×10^4
Cow	1.02×10^7	2.21×10^7
Pig	2.57×10^6	3.66×10^7
Sheep	3.02×10^5	2.67×10^8
Goat	1.16×10^7	1.21×10^8
Rabbit	1.55×10^6	8.50×10^7
Goose	1.35×10^7	1.10×10^7
Turkey	5.17×10^8	5.39×10^7
Duck	9.28×10^7	1.06×10^8

As shown in Table 4, although human feces contain large numbers of bifidobacteria, high levels can also be recovered from domestic and wild animals. Beerens (1991) was able to isolate Bifidobacterium spp. from the domestic rabbit, horse, chicken, swallow, crow, domestic rat, dog, pig and fox as well.

Diet appears to play an important role in bifido colonization. Trovatelli and Matteuzzi (1976) studied the numbers and species of bifidobacteria present in the rumen of calves fed high-roughage and high-concentrate diets. They found that bifidobacteria were not detectable in a 10^{-3} dilution with the roughage diet, whereas with the high-carbohydrate concentrate ration their numbers were generally in the order of 10^{8} to 10^{9} per mL of rumen fluid. *Bifidobacterium ruminale* and *B. globosum* were the species most frequently isolated.

Our previous work (Seyfried *et al*., 1990) showed that *B. adolescentis* and *B. breve* were the predominant species in human feces and sewage. Carrillo and co-workers (1985) also found that *B. adolescentis* was isolated most frequently (88.9% of the 105 isolates) from tropical freshwater samples, followed by *B. angulatum* (5%), *B. infantis* (5%) and *Bifidobacterium* spp. (unknown) (1.1%).

Mara and Oragui (1983) have suggested that sorbitol-fermenting bifidobacteria, such as *B. adolescentis* and *B. breve*, be used as human fecal pollution indicators. This proposal has merit but, due to the fact that *B. adolescentis* has been isolated from dogs and *B. breve* from chickens (Seyfried *et al*., 1990), further studies are required.

CONCLUSION

The EC:SC ratio shows promise as a method of indicating human or animal sources of pollution.

Bifidobacterium species are present in high levels in human fecal material but high densities also occur in animal feces. More research is needed to determine if the species are human or animal specific.

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VOLUME II

SESSION D

EMISSIONS AND EFFLUENTS

POSTER PRESENTATIONS

DP1

GEOCHEMICAL CHARACTERIZATION OF METAL/PARTICULATE ASSOCIATIONS IN 3 OUTFALL TYPES TO THE DON RIVER.

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Reductions of suspended solids and metals are important components in water quality remediation of the Toronto Area Watershed. Despite the fact that the majority of metals end up in association with particulates, solids reduction will not necessarily lead to trace metal reductions - particularly reductions in potentially bioavailable trace metals. Sediment geochemistry is of primary importance in determining trace metal partitioning; and depending on which geochemical fractions are involved (*e.g.* oxides, clays, organics), metals may be bound, only to be released again given changes in system chemistry. We have been evaluating trace metal transport by suspended sediments in the Don River over the last 3 years. There is a considerable amount of univariate deviation in these results which is not surprising given the myriad contaminant sources and the hydrologic regime of the Don. However, multivariate analysis of these data indicate that the geochemical phase of the particulates combined with information on dissolved salts *e.g.* Cl^- and Ca^{2+}, explain a large proportion of that variance. By examining specific types of discharge sources, the relative influence of those sources for *in situ* river patterns of trace metals/suspended sediment associations can be determined. Such a relationship may be a means of "fingerprinting" specific discharge sources to the Don. Prioritization of source abatements and the effectiveness of proposed remedial action plans can then be objectively evaluated. We are assessing the trace metal/suspended sediment associations of 3 outfall types on the Don (STP, "residential" and "industrial"). Outfall samples are sized, and metals (Cd, Cu, Zn and Pb), associated with 4 operationally defined sediment geochemical fractions (exchangeable, oxides, organics, and resistate minerals) are extracted, and subsequently analyzed by flame atomic absorption.

DP2

MONITORING AIR POLLUTION SOURCES (MAPS)

MAPS Mobile Stack Emissions Monitoring Laboratory

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Gary Wong
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THE MAPS Mobile Laboratory (MAPS) is a 30' Orion bus fitted with continuous emission monitors and all associated equipment (sample conditioners, pumps and transport systems, data acquisition and processing systems, etc..) to continuously measure stack gas concentrations of oxygen, carbon dioxide, carbon monoxide, hydrocarbons, nitrogen oxides, sulfur dioxide, total reduced sulfur and hydrogen chloride. External devices to measure other emission factors such as opacity, stack temperature, and flow rates are also present.

The MAPS is utilized by the Air Resources Branch, Source Assessment & Technology Unit to conduct continuous emission measurements at stationary sources, perform audits on continuous emission monitoring systems, and to provide support to special emission characterization studies. The information gathered is essential in assessing stack monitoring systems' performance, efficiency of emission abatement equipment, and compliance with emission standards.

In the past year, MAPS has conducted source monitoring surveys at London Victoria Hospital's Energy from Waste plant to audit the performance of their continuous emission monitoring system, took part in the Ministry's Recycled Tire/Rubberized Asphalt project by providing continuous emission measurements of conventional and rubberized asphalt production at two Ontario asphalt plants, and assessed compliance with oxygen, total hydrocarbon, and carbon monoxide emission standards at the Smithville CWML Decontamination Site incinerator.

In order to meet the needs of its ever expanding mandate, the MAPS Mobile Laboratory is continually updated with state-of-the-art equipment to increase the unit's versatility, and to assure monitoring data accuracy and completeness. The MAPS Mobile Laboratory provides an essential service to the Air Resources Branch and the Ministry's Regional staff.

DP3

SOURCE CHARACTERIZATION OF EMISSIONS FROM RESIDENTIAL WOOD BURNING

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INTRODUCTION

The increased use of residential wood combustion in Ontario and several other areas of North America has resulted in adverse air quality impacts in some areas. A recent literature review of such impacts and of the legislative approaches directed at minimising such impacts, pointed to the need for the characterization of the organic and inorganic components in residential wood stove emissions from typical firewood and stoves used in Ontario. The source characterization study will be followed by a monitoring program designed to indicate the ambient air quality impacts of residential woodburning in selected communities in Ontario.

Most of the earlier work on source characterization focused on inorganic components and organic carbon. Recently, source profile information on organic components especially polynuclear aromatic compounds is being determined. The influence of stove type, fuel (wood) type and condition, and of woodstove operating conditions on source profiles represent formidable challenges in reliably characterizing source profiles. Source testing in the present study was designed to measure emissions during steady state burning using three stove commonly used in Ontario and using maple, birch and jackpine firewood - three of the commonly used firewoods in Ontario.

This presentation outlines the preliminary results of the source testing of emissions from three wood stoves (designated A, B and C) and three types of wood. The primary objective of the testing is to obtain source profiles (for organic and inorganic species) for three typical fire woods and wood stoves used in Ontario. Source testing was completed in mid-September and preliminary results for the organic components analyzed are discussed here. Analytical data for inorganic species were unavailable of the time of writing.

METHODS

The test facility was located at the University of Waterloo, Department of Mechanical Engineering. Well cured and dried firewood obtained from commercial suppliers was stored indoors at the test facility. A 4" flue was attached to each stove and the exhaust gases were vented through existing exhaust ducts in the laboratory. A sampling port was located 2 m from the base of the stove exhaust. A modified Ontario Ministry of the Environment (OME) Method 5 sampling train (NAPP Inc. Model 63) was used to obtain samples of emissions. Standard protocols were established to conduct each test to ensure consistent stove operation. For each test, the stove was allowed to reach a steady state condition representative of steady burning conditions. At least duplicate tests were conducted on each woodstove/wood combination.

All test materials (filters, solvents and sorbents) were analyzed prior to the initiation of tests. All target analyte compounds had acceptable blank levels. The sampling train consisted of a heat traced probe with a nickel plated stainless steel nozzle, and attached thermocouple and pitot tube. After the probe, the gas passes through a cyclone, a heated filter holder (glass fibre filter) and a sorbent module containing XAD-2 resin. Four impingers are downstream of the sorbent module; the first two impingers contained HPLC grade water, the third was empty and the fourth contained silica gel. The impingers are followed by a pump, dry gas meter and a calibrated orifice meter.

Proofs of the sampling train and blank filters also acceptable blank levels for all analytes. Single point non-isokinetic sampling was carried out for approximately 50 to 80 minutes to obtain a sample volume of 0.6 to 1 m^3 (dry standard cubic metre (DSCM)). The precise sample volume for each run was calculated. Traditional measurements throughout the run of flue gas velocity, temperature, volume and pressure were made. Since the flow rates from wood stoves are so low, and because the majority of particulate emissions occur in the very fine size fraction (< 2.5 µm diameter), non-isokinetic sampling was considered adequate for meeting the objectives of this study. The particulate fraction was collected on a glass fibre filter and the semivolatile organics were collected on XAD-2 resin. Samples of stack gas were collected in tedlar bags for analysis of CO and CO_2.

The sampling train was analyzed as three fractions as follows. The rinse from the front half (nozzle, probe liner and cyclone) together with the first three impingers were combined and analyzed as the first fraction. The filter (one half) and the resin were analyzed separately as the second and third fractions. Each fraction was soxhlet extracted in dichloromethane, solvent exchanged in cyclohexane and then extracted with toluene and analyzed by GC/MS for 24 organic species including 16 PAH. The filter was analyzed by ICP for 21 elements.

RESULTS AND DISCUSSION

The total mass of each component in the sample was calculated by summing the masses in each of the three fractions analyzed. There were negligible amounts of analytes in the probe rinse and impinger fraction; the majority of the constituents were present in the resin. The negligible amount in the probe and impinger fraction indicates that most of the organic species are present on the vapour phase and that negligible amounts of organics are present in larger particles which would be deposited in the probe.

The concentration of each species was calculated from the total mass and the corrected (to standard dry gas volume at 25 °C and 1 atmosphere) sample volume. The source profiles are expressed as the ratio of each component relative to the concentration of benzo(a)pyrene.

Within each stove type the profiles were most consistent for the heavier PAHs - perylene, indeno(1,2,3,c-d)pyrene, dibenzo(a,h)anthracene, benzo(e) and benzo(a)pyrene. The lighter and more volatile PAH (anthracene, fluorene, phenanthrene) showed greater variability in their profiles. Stove B gave most consistent results even for the more volatile compounds.

The profiles for each wood type showed no major differences suggesting that wood types and stove types used have no dramatic influence on the source profiles for the components measured in this study.

CONCLUSIONS AND RECOMMENDATIONS

More detailed examination of test conditions and analysis of the inorganic data will take place before firm conclusions are drawn regarding the influence of stove type and wood on the source profiles.

VOLUME II

SESSION E

ENVIRONMENTAL TECHNOLOGIES PROGRAM

VERBAL PRESENTATIONS

TOXIC CHEMICAL
SPECIALISTS

ECO LOGIC

DEMONSTRATION TESTING OF A THERMAL GAS PHASE REDUCTION PROCESS

BY

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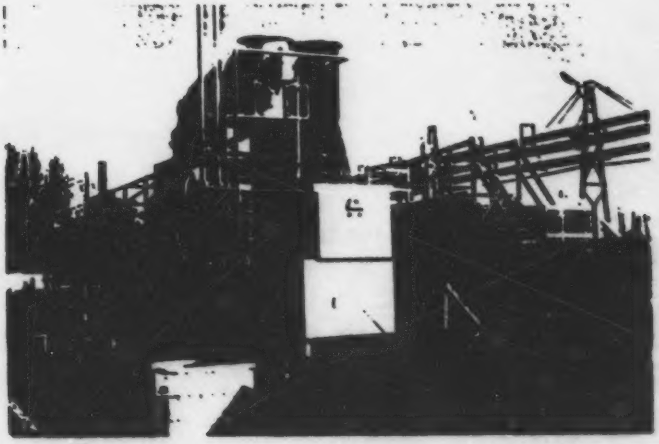

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1.0 INTRODUCTION

ECO LOGIC has been conducting research on a method of decontaminating hazardous wastes using a patented thermo-chemical reduction process. This process is particularly suitable for wastes that are primarily aqueous, such as harbour sediments, landfill leachates and lagoon sludges. The research to date has been funded by the National Research Council Industrial Research Assistance Program, the Defence Industrial Research Program administered by the Department of National Defence, the Great Lakes Clean Up Fund, the Ontario Ministry of the Environment, the Environmental Technologies Program and ECO LOGIC.

Research and development has focused on bench-scale testing of surrogate compounds, development of a larger lab-scale destructor for testing actual waste samples, and construction of a mobile full-scale field unit for materials and component testing.

2. BACKGROUND

There is a growing sense of awareness and concern about the state of our environment and the lack of appropriate ways of dealing with some of the problems we have created. ECO LOGIC was formed in 1986 specifically to address the need for a clean-up tool for one of the most difficult problems, that of severely contaminated aqueous wastes such as harbour sediments, landfill leachates, and lagoon sludges. A technology that could also address stored waste problems such as contaminated soils, contaminated solvents and oils, pesticides, chemical warfare agents, and industrial effluents was considered most desirable. The criteria that ECO LOGIC used in developing the process included:

- destruction efficiency
- possibility of dioxin or furan formation
- continuous monitoring and process control suitability
- suitability for aqueous wastes
- mobility
- cost

The patented ECO LOGIC process addresses all of these criteria. It is based on the gas-phase thermo-chemical reaction of hydrogen with organic and chlorinated organic compounds at elevated temperatures. At 850°C or higher, hydrogen reacts with organic compounds in a process known as reduction to produce smaller, lighter hydrocarbons. In the case of chlorinated organic compounds, such as polychlorinated biphenyls (PCBs), the products of the reaction are primarily methane and hydrogen chloride. This reaction is enhanced by the presence of water, which can also act as a reducing agent. Bench-scale testing with trichlorobenzene (half of a PCB molecule) has shown that the reduction reaction will achieve 99.9999% destruction efficiency or better. The first measure of a good destruction technology is high destruction efficiency, and the bench-scale testing demonstrated that the ECO LOGIC process was capable of this.

2.1 Thermo-Chemical Reduction Reactions

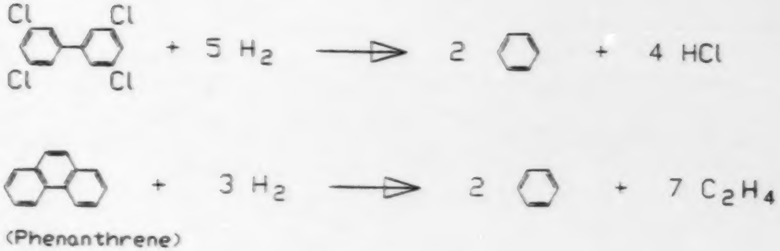
Figure 1 shows the six principal reduction reactions that occur in the ECO LOGIC process. The first is the dechlorination and dismantling of a PCB molecule to produce hydrogen chloride and benzene. The second is the reduction of a polyaromatic hydrocarbon (PAH) compound, phenanthrene, to produce benzene and ethylene. The third reaction is the reduction of a benzene molecule to produce ethylene, and the fourth is the reduction of ethylene to produce methane. The fifth reaction is the reduction of straight-chain hydrocarbons to produce methane. The sixth reaction is known as the water shift reaction and is not a reduction reaction, although it occurs only in a reducing atmosphere. In this reaction, methane and water combine to form carbon monoxide and hydrogen.

All of these reactions occur simultaneously in the ECO LOGIC process, although to varying degrees and at various rates. The most efficient and fastest reactions are the dechlorination of chlorinated organics and the reduction of multi-ring structures to form benzene. The reduction of benzene to ethylene and the reduction of ethylene to methane occur at roughly the same rate and conversion efficiency, approximately 99%. Straight-chain compounds convert to methane at a higher rate. The result is that about 99% of the organic material input to the process is converted to methane and virtually all the rest is converted as far as ethylene or benzene.

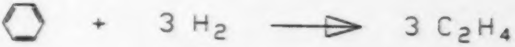
The back reaction from methane in combination with water to form carbon monoxide and hydrogen is much less efficient (20-30%) but, nonetheless, very useful. Since hydrogen is one of the main costs of operation, reactions which generate hydrogen help reduce the overall cost of the process. Unfortunately, this reaction and the conversion of ethylene to methane are both endothermic, so there is an increased energy cost which partially offsets the savings on hydrogen. Another hydrogen-producing reaction is the breakdown of methane to form carbon and hydrogen. This occurs to a limited extent depending on the amount of excess hydrogen in the reducing atmosphere and the reaction temperature.

FIGURE 1

THERMO-CHEMICAL REDUCTION REACTIONS


Cl
Cl
Cl
Cl
+ 5 H2
2
+ 4 HCl
+ 3 H2
2
+ 7 C2H4

(Phenanthrene)



$$C_2H_4 + 2\ H_2 \longrightarrow 2\ CH_4$$

$$C_nH_{(2n+2)} + (n-1)\ H_2 \longrightarrow n\ CH_4$$

WATER SHIFT REACTION

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

The second criterion for process design was elimination of the possibility of dioxin and furan emissions. Because the ECO LOGIC process uses reduction reactions, it is not an incineration technology. Incineration processes destroy chlorinated organic wastes by breaking contaminant molecules apart with high temperatures and then combining them with oxygen, usually from air. A PCB waste first fragments to form chlorobenzenes that can combine with oxygen to form dioxins and furans, which are more toxic than the original PCBs. The ECO LOGIC process uses hydrogen to produce a reducing atmosphere devoid of free oxygen, and thus eliminates the possibility of dioxin or furan formation.

Other non-chlorinated hazardous organic contaminants, such as PAHs, are also reduced by the ECO LOGIC process to smaller, lighter hydrocarbons, primarily methane and ethylene. Because of the tendency of the reaction to produce lighter, more volatile gases, the process leads itself to continuous monitoring of the destruction efficiency. This satisfied the third criterion of process design. ECO LOGIC has purchased a very sophisticated on-line mass spectrometer process gas analyser system which is capable of measuring many organic chemicals on a continuous basis. It was used for bench-scale and lab-scale testing, and is now part of the process control system in the pilot-scale demonstration unit. PCB and PAH destruction efficiencies can be measured very quickly by continuously monitoring chlorobenzene and benzene concentrations. The information from the mass spectrometer is sent to the process controller so that an increase in chlorobenzene or benzene concentration (signalling a decrease in PCB or PAH destruction efficiency) halts the input of waste and alerts the operator.

The fourth measure of a destruction technology is its ability to process aqueous wastes. The ECO LOGIC process is suitable for many types of waste, including those with a high water content which are very difficult to incinerate. For example, water contaminated with 0.1% (1000 ppm) PCBs can be processed easily with this reaction. The presence of water in the waste actually aids in the destruction process since water itself can act as a reducing agent to help dismantle the contaminant molecules.

The final criteria ECO LOGIC used in designing the process were mobility and cost. Because the process is not an incinerator, the reactor does not require a large volume for the addition of combustion air. The small reactor size and the capability to recirculate product gases from the reaction make the process equipment small enough to be mobile. As well, the smaller size reduces the capital cost of the process equipment. The main processing costs are for hydrogen, electricity, and personnel. A commercial-scale system processing 100 tonnes per day should be capable of operating for a price of approximately $500 per tonne of waste processed. This is roughly equivalent to the cost of long-term entombment, with the advantage of actually eliminating the problem.

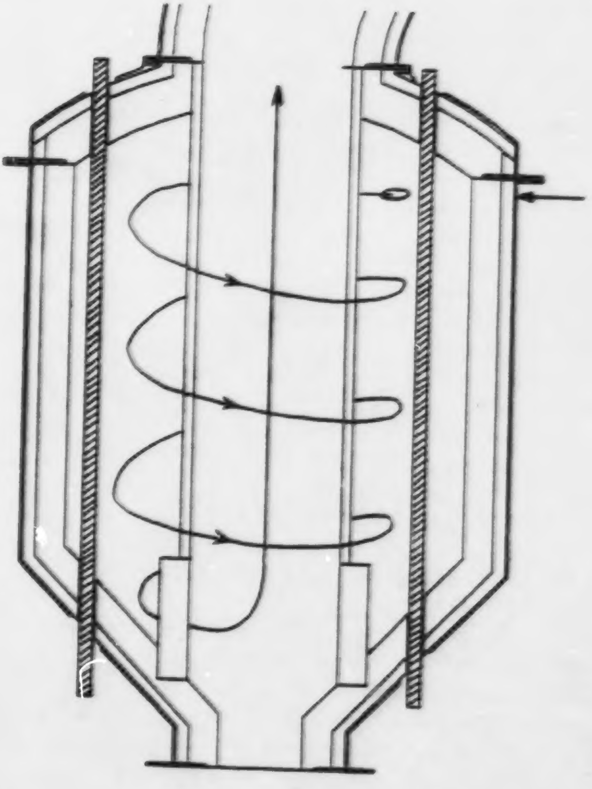
The research and development required to produce a working pilot-scale model of the process proceeded along four fronts. Bench-scale testing proved the chemical reduction reactions would work with pure compounds with or without the presence of water, and established parameters for residence time, temperature, and appropriate ratios of hydrogen to waste. These tests were conducted at a small scale using laboratory glassware and a quartz tube furnace as a reactor. A larger lab-scale reactor was used to process 5-10 litre quantities of actual waste samples, primarily harbour and lagoon sediment samples. This established the capability of the process to deal with actual wastes in complex matrices. During the bench-scale and lab-scale work, a third thrust of research was the development of a computer model to simulate the operation of a pilot-scale reactor system and to aid in the design of such a system. The fourth phase of research was the construction and proof-of-concept testing of the pilot-scale reactor system. This phase included materials and component testing for coping with a hydrogen- and acid-rich high-temperature reducing atmosphere, and system integrity testing to ensure that the system could achieve temperatures, flowrates and pressures during leak-free operation.

2.2 Pilot-scale Reactor System

Figure 2 shows a schematic of the reactor designed to accommodate the thermo-chemical reduction reaction. A mixture of preheated waste and hydrogen is injected through nozzles mounted tangentially near the top of the reactor. The mixture swirls around a central ceramic

FIGURE 2

THERMO-CHEMICAL REDUCTION REACTOR



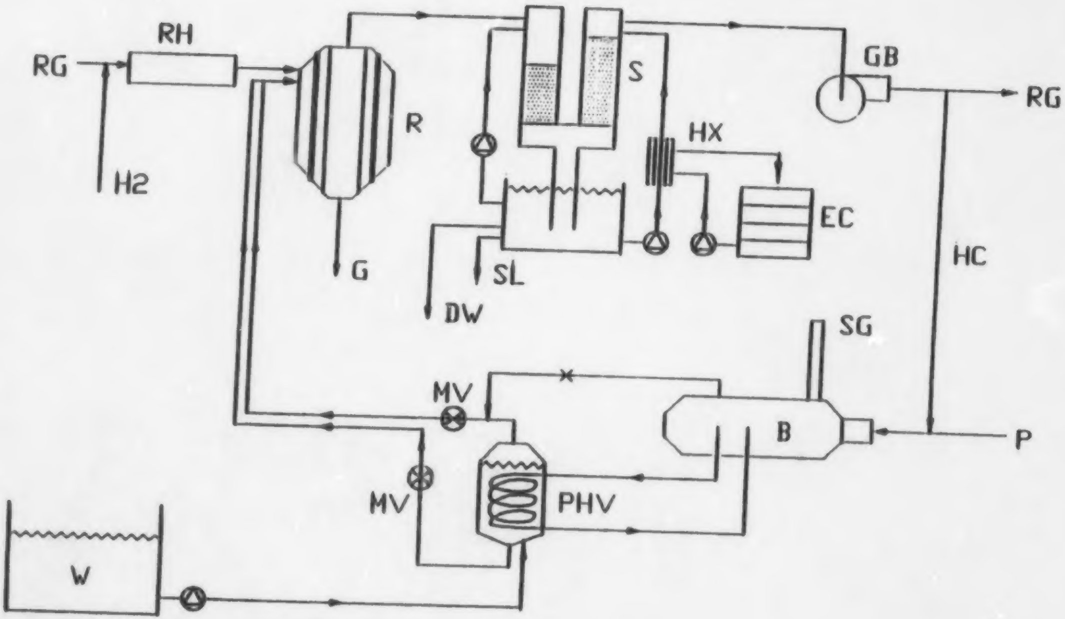
tube past glo-bar heaters and is heated to 850°C by the time it passes through the ports at the bottom of the ceramic tube. Particulate matter up to 5 mm diameter not entrained in the gas stream impacts the hot refractory walls of the reactor, thereby volatilizing any organic matter associated with the particulate. That particulate exits out of the reactor bottom to a quench tank, while finer particulate entrained in the gas stream flows up the ceramic tube into the exit elbow and through the retention zone. The reduction reaction takes place from the bottom of the ceramic tube onwards, and takes less than one second to come to completion.

Figure 3 shows a complete process schematic of the field demonstration unit, which operated at Hamilton harbour. Waste liquid and suspended solids were pumped from a small storage tank (W) to a heat exchanger vessel (PHV) for preheating to 150°C by a small boiler (B). Hot liquid and steam from the watery waste were metered continuously using special metering valves (MV) and injected into the reactor (R) using atomizing nozzles. A mixture of hydrogen (H_2) and recirculation gas (RG) also entered the reactor near the top after passing through a gas-fired heat exchanger (RH). Heavy particulate was removed as grit (G) out the bottom to a quench tank and fine particulate and gases passed up the ceramic tube where the gas-phase reduction reaction took place. Additional residence time was provided by the retention zone elbow and extension pipe prior to the scrubber. Once the gases entered the scrubber (S), they were quenched by direct injection of scrubber water spray. Hydrogen chloride and fine particulate were removed by contact with the scrubber water as the gases passed through the scrubber media. Scrubber water was collected in a tank below via a large water-sealed vent that also acted as an emergency pressure relief duct. The scrubber water was cooled to 35°C using a heat exchanger fed by cooling water from an evaporative cooler (EC). Sludge (SL) and decant water (DW) were the two effluent streams from the scrubber and both were held in tanks for batch analysis prior to disposal.

The gases that left the scrubber consisted primarily of excess hydrogen, reduction products such as methane and ethylene, and a small amount of water vapour. Approximately 95% of this gas was recirculated back into the reactor after reheating to 500°C, and about 5% of the hydrocarbon-rich gas (HC) was used as supplementary fuel in the boiler. The boiler used propane (P) as its main fuel to produce steam used in the heat exchanger which preheated the

FIGURE 3

PROCESS SCHEMATIC


RG
RH
H2
R
G
S
SL
DW
HX
EC
GB
RG
HC
SG
MV
MV
PHV
B
P
W

waste to 150°C. The only air emissions were from the boiler in the form of stack gas (SG). Since the fuel going into the boiler was very clean and contained no chlorine, emissions from the boiler were insignificant.

The process gas was sampled continuously using an on-line mass spectrometer gas analyser system. A sample was drawn form a location just prior to the scrubber through heated lines to the analyser. In the case of a process upset where total destruction of hazardous organic compounds was not occurring, the on-line mass spectrometer automatically divert all gases into a recirculation mode. Under these conditions, no sidestream gas (HC) would be sent to the boiler and the waste feed would be curtailed. Recirculation would continue until the continuous analysis indicated the reaction was again occurring optimally. During this time, no escape of or incineration of chlorinated organic compounds would occur. During the Hamilton harbour demonstration program, this safety feature was never called upon, but the on-line mass spectrometer proved very useful in evaluating process conditions, changes in feed composition, and destruction efficiency.

The equipment described above was commissioned at Hamilton Harbour on two 45-foot drop-deck trailers. A process control trailer containing the on-line mass spectrometer, process control system, and other analysis equipment was located near the two process trailers. Figure 4 shows a plan view of the pilot-scale reactor system layout as it was set up at Hamilton Harbour. The footprint for the entire process was only 20m by 60m. The equipment was completely self-contained with its own power generator and water supply. Table 2 lists the types of wastes tested at Hamilton Harbour and at bench-scale and lab-scale.

FIGURE 4

PILOT-SCALE REACTOR SYSTEM LAYOUT

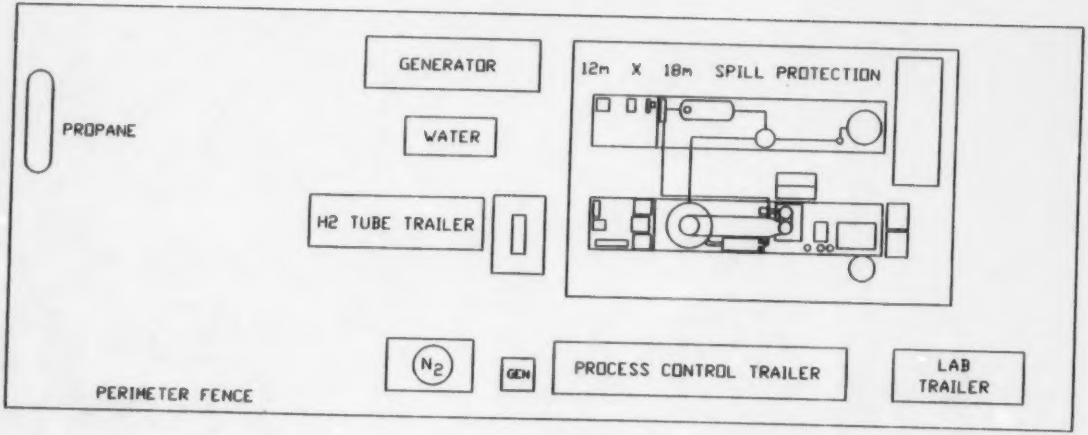

PROPANE
GENERATOR
WATER
H2 TUBE TRAILER
12m X 18m SPILL PROTECTION
N2
GEN
PROCESS CONTROL TRAILER
LAB TRAILER
PERIMETER FENCE

TABLE 1 WASTES TESTED TO DATE

1)	Pure Compounds	(Bench Scale) PCB askarel (Aroclor 1254) Hexachlorobenzene Trichlorobenze 2,4-D Methoxychlor
2)	Environmental Wastes	(Laboratory Scale) (1 Kg/hr)
	Hamilton Harbour Sediment	(coal tar, PAH, TCB, Fe, Zn)
	Thunder Bay Harbour Sediment	(chlorophenols, wood treatment waste)
	Sheboygan Harbour Sediment	(PCBs)

(Audited Program by Environment Canada)

3)	Full Scale Testing	(2 - 5 kg/min)
	Hamilton Harbour Sediment	(3 - 7 T/day coal tar, PAH, Fe, Zn) (3 T/day as above spiked with 110 ppm PCBs)

(Audited Program by Environment Canada and the Ontario
Ministry of the Environment)

PROPOSED DEMONSTRATION FOR FALL 1991

1)	US EPA SITE demonstration	(3 - 5 kg/min)

Composite mixture of liquid PCB, TCE, DCM, and other chlorinated liquids pumped from a municipal landfill.

3.0 GENERAL STRATEGY

ECO LOGIC will enter the market to supply hazardous waste destruction services itself with its own machines, and to licence and sell equipment to companies that already supply services, or to licence and sell to large chemical producers or users where ownership is economically advantageous. The service market is the initial focus in order to demonstrate the machine and obtain approvals in jurisdictions where units will be licensed and sold when the technology has buyer (versus user) acceptance.

We would encourage interested parties with organic hazardous waste problems to contact our offices in Rockwood and Ann Arbor. Wastes suitable for destruction using the Eco Logic process are listed in Table 2.

This offers potential clients the opportunity to obtain direct information on the application of this technology to the resolution of their hazardous waste problems.

For more information, please do not hesitate to contact:

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Vice President
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ELI Eco Logic International Inc
2395 Huron Parkway
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313-973-2780

Jim Nash, B.A.
Manager
Sales & Business Development
ELI Eco Logic International Inc
143 Dennis Street
Rockwood, Ontario Canada N0B 2K0
519-856-9591

TABLE 2 WASTES SUITABLE FOR DESTRUCTION

CHEMICALS:

Non-halogenated / halogenated biphenyls
Non-halogenated / halogenated benzenes
Non-halogenated / halogenated phenols
Non-halogenated / halogenated cycloalkanes
Non-halogenated / halogenated alkanes
Non-halogenated / halogenated dioxins
Non-halogenated / halogenated dibenzofurans
Polyaromatic hydrocarbons

* Note: Halogenated means: Chlorinated
Brominated
Fluorinated

TYPICAL WASTES:

PCBs
Pulp mill wastes
Chlorinated solvent waste
Contaminated coal tars
Solvent still bottoms
Chlorophenols / Wood treatment waste
Pesticide wastes
Landfill leachates
Lagoon bottoms

SEALABLE JOINT SHEET PILE CUTOFF WALLS FOR PREVENTING AND REMEDIATING GROUNDWATER CONTAMINATION

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INTRODUCTION

The Institute for Groundwater Research (IGR) at the University of Waterloo is developing a new type of steel sheet piling specifically for use as low permeability cutoff walls. These walls are used for controlling the migration of contaminated groundwater and for enhancing the effectiveness of subsurface remedial measures. This new sheet piling differs from conventional sheet piling in that it has joints that can be sealed after the wall has been driven into the ground, and is known as Waterloo Sealable Joint Sheet Piling, or SJSP.

BACKGROUND

Low permeability cutoff walls are commonly used for minimizing the spread of contaminated groundwater at sites such as landfills, waste lagoons, or industrial sites that have on site contaminant sources. Cutoff walls function as low permeability barriers and slow the rate of groundwater advection. The rate of advection through a wall is directly proportional to the permeability and difference in hydraulic head across the wall, and inversely proportional to the thickness of the wall.

There are two wall configurations in profile. Keyed walls extend from ground surface into a low permeability layer, such as clay or silt, that ideally is continuous across the site. Hanging walls do not extend into a low permeability layer at depth. Water can flow beneath a hanging wall, so water levels must be controlled via pumping wells upstream of the wall to prevent advection of contaminated groundwater beneath the wall. However, hanging walls can be used effectively without pumping wells or with very little pumping for preventing migration of liquids that spread near the water table, such as petroleum products, and for preventing migration of soil vapours.

In plan view, the most effective wall configuration is one that completely encircles the zone to be isolated. Non-encircling walls are commonly used, but a network of pumping wells for controlling water levels is necessary for preventing contaminated groundwater from deflecting around the ends, similar to the way that pumping wells are necessary for preventing contaminated groundwater from flowing beneath a hanging wall.

Cutoff walls have long been used in geotechnical applications for minimizing the flow of groundwater into excavations and underflow beneath dams and levees. Cutoff walls are also used for environmental control purposes, typically for either controlling a plume of contaminated groundwater or for isolating a source of groundwater contamination. With a growing awareness of the limitations of pump-and-treat programs for remediating aquifers (Mackay and Cherry, 1989), there is likely to be more emphasis placed on isolating the source of contamination as a control means. Cutoff walls are ideally suited for source isolation.

Cutoff walls can also be used for enhancing the effectiveness of other site remediation techniques. For example, a keyed cutoff wall enclosure was used for isolating an area where surfactant flushing was used for removing DNAPL from a sandy aquifer (Fountain, 1991). In this application the cutoff wall provides hydraulic control, which minimizes adverse effects due to dilution and prevents migration of fluids away from the remediation area. Cutoff walls can be used for making other remedial techniques feasible. For example, the water table inside an encircling wall can be lowered, and vacuum extraction used for removing volatile organic liquids from the pores.

IGR researchers became interested in cutoff wall construction techniques because there was a need to isolate portions of an aquifer for experimental purposes. We were unable to identify a technique that we were confident would perform satisfactorily, and that could be economically constructed at the relatively small scale required. Compared to the size of a typical cutoff wall project, the walls required by IGR were tiny, and mobilization and setup costs were a substantial portion of the total cost. Walls of a similar size would be very useful for surrounding localized contaminant sources, and for installation in a precautionary mode where spills or leaks of hazardous materials are likely to occur, such as at liquid storage or transfer facilities. Our experience suggests that small installations like these would be relatively expensive if constructed using conventional technology, and hence would not be likely to be built due to the lack of a cost effective technique. However, if a relatively inexpensive, reliable technique for constructing cutoff walls at a small scale was available, areas where spills or leaks are likely to occur could be practically isolated. This would decrease the incidence of groundwater contamination and the liability arising from spills or leaks due to routine operations.

Starr and Cherry (1990) describe a variety of techniques for constructing cutoff walls. In slurry trench methods, a trench is excavated while being kept filled with a suspension of clay and water, which prevents the walls of the trench from collapsing. The trench is either backfilled with a mixture of native soil and bentonite (a soil bentonite wall), or the slurry is amended with Portland cement, which hardens to form a low permeability element (a cement bentonite wall). In grouting techniques, a low permeability material is injected into the ground. Grouting methods include the vibrated beam technique, in which a steel beam is driven into the ground to create a cavity into which grout is injected as the beam is withdrawn, conventional pressure grouting, and jet grouting, in which high velocity jets mix grout with the soil surrounding a borehole to form 'soilcrete' columns or panels. Membrane walls are formed by inserting a low permeability sheet, typically high density polyethylene, into the subsurface.

Conventional steel sheet piling is sometimes used for making cutoff walls for environmental control purposes. However, the use of conventional piling is limited because the open joints between adjacent sheets allow too much water to leak through. Over time, leakage through joints may decline as the joints become clogged as soil is washed in, or as corrosion of the steel blocks the joints with rust. Blockage of joints by these mechanisms is not reliable, so they should not be depended upon for making conventional sheet piling acceptable for environmental control purposes. Obviously, a better situation would be if the joints could be sealed directly.

DEVELOPMENT OF SEALABLE JOINT SHEET PILING

Researchers at the Institute for Groundwater Research have developed steel sheet piling that incorporates joints that can be filled with a sealant after the sheet piles have been driven into the ground (patent pending: E.S. Vales, University of Waterloo). Prototype sealable joint sheet piling was constructed by attaching a steel L section, or an angle iron, to conventional sheet piling. Angle irons were welded to sheet piles to form a cavity adjacent to each joint (Figure 1). The bottom of each angle iron is fashioned in such a way that very little soil enters the joint as the sheets are driven. After the sheets are driven to the required depth , the cavities are flushed to remove any foreign matter and then filled with sealant.

Field trials of cutoff walls constructed with prototype sealable joint sheet piling, which are described in the next section, were successful. These trials indicate that sealable joint sheet piling is feasible from a technical viewpoint. Attaching angle irons to every joint is costly. A less expensive technique for producing a sealable joint would improve the economic feasibility of sealable joint sheet pile cutoff walls. A new joint that provides space for sealant inside the joint itself was designed, which eliminates the need for attaching angle irons at each joint. The modified joint (Figure 2) is formed at the same time that the sheet piling is roll formed, so the additional cost of a sealable joint over a conventional joint is minimal.

The tooling necessary for roll forming a sheet pile section that incorporates the modified joint has been manufactured and installed at a rolling mill. The first production run is scheduled for late October, 1991. The modified sheet piling produced in this first run will be used for field and laboratory performance evaluations, which are scheduled to begin in November.

An important component of this project is selection of sealants that will perform in a variety of subsurface conditions. A joint sealing compound must have low permeability, must bond well to steel after having been emplaced under water, and it must withstand chemical attack by the natural groundwater and any contaminants that are present. It must also withstand freeze-thaw cycles and deformation of the wall due to earth movements. Bentonite based grouts and a proprietary polymer (Dow Chemical) have been used successfully in field tests to date. Additional sealant materials are being evaluated.

FIELD TRIALS

Cutoff walls are generally not constructed in a configuration that allows meaningful field measurement of hydraulic conductivity, so there are few reports of the actual performance of conventional cutoff walls. Estimates of the hydraulic conductivity of cutoff walls are typically based on laboratory measurements using samples of materials used for constructing the wall or samples actually collected from the wall. The as-built performance of a wall depends largely on the presence of imperfections in the wall, which laboratory measurements do not address.

In contrast to the usual situation, several cutoff walls have been constructed by IGR in a configuration that allows meaningful field measurement of hydraulic conductivity. In each case, the test facility is a square or rectangular box, whose walls consist of sealable joint sheet piling. Several test cells have been built at an IGR research site at Canadian Forces Base

Borden. Hydraulic tests have been conducted, and then the cells have been used for other experiments. The cells typically extend through a 3.5 m thick surficial aquifer and 0.5 m into the underlying aquitard, although cells have been constructed to a depth of 11 metres. The aquitard provides a good bottom to the cell, which is necessary for a hydraulic test to be conducted. Another test cell has been built in the clay plains of southwestern Ontario and hydraulically tested. The upper portion of the subsurface at this site is relatively permeable, and the underlying portions are less permeable. The walls of the test cell extend into the low permeability material at depth, which again forms a good bottom to the cell.

To conduct a hydraulic test, the water level inside the cell is displaced from the equilibrium value and the rate at which the water level returns to equilibrium is observed. The rate of water level change depends on the size and shape of the cell, the thickness of the wall, the head difference across the wall, and the permeability or hydraulic conductivity of the wall. The field results are compared with a mathematical model that assumes that water flows uniformly through the entire wall, but not beneath the wall. This yields a single value of hydraulic conductivity for the entire wall, K_{bulk}.

Hydraulic tests of the first cell were conducted before and after the joints were sealed with a bentonite grout. The test conducted before the joints were cleaned or sealed indicates a bulk hydraulic conductivity of 10^{-4} cm/s. Sealing the joints reduced the hydraulic conductivity to 10^{-7} cm/s, or 0.1% of its initial value. This clearly demonstrates the effectiveness of joint sealing in improving the performance of a sheet pile cutoff wall. A larger cell was built using the same style of prototype sealable joint sheet piling and sealed with an improved bentonite grout mixture. The hydraulic test of this cell indicates a hydraulic conductivity of 10^{-8}cm/s.

The test cell in southwestern Ontario was sealed with an organic polymer instead of bentonite grout. The hydraulic test of this cell indicates that the bulk hydraulic conductivity of the wall is between 10^{-9} and 10^{-10} cm/s (Figure 3). There are several differences between this test cell and those at CFB Borden, so it is not valid to conclude that the organic polymer is necessarily a better sealant than bentonite grout. Additional tests at CFB Borden are underway to facilitate this comparison. Nevertheless, the hydraulic tests of the large cell at Borden and the southwestern Ontario cell are quite encouraging, yielding bulk hydraulic conductivity values that are low enough to be acceptable for many environmental control applications.

In jurisdictions lacking regulations that specify a required hydraulic conductivity for cutoff walls, it is common practice to apply US EPA requirements for soil based landfill liners, which require a hydraulic conductivity of 10^{-7} cm/s or less. The State of California requires that cutoff walls at waste disposal sites have a hydraulic conductivity of less than 10^{-6} or 10^{-7} cm/s, depending on the wastes disposed at the site, and a thickness of 0.61 m (California Code of Regulations, 1990). If cutoff wall performance is compared on the basis of the amount of water that flows through a unit area of wall per unit time, i.e. the flux through the wall, then the thickness of the wall and the hydraulic conductivity must be taken into account. Two walls that have the same ratio of hydraulic conductivity to thickness will transmit the same flux through the wall, for the same difference in hydraulic head across the wall. Thus, a SJSP wall 1 cm thick with a hydraulic conductivity of 1.7×10^{-9} cm/s would be equivalent to a wall that meets the more stringent California criteria.

POTENTIAL USES AND ADVANTAGES OF SEALABLE JOINT SHEET PILE CUTOFF WALLS

Waterloo sheet pile cutoff walls have many applications, including:

- shallow containment of spills of lighter-than-water petroleum products, where the wall would be driven to a depth below the water table sufficient to stop the lateral spread of free product near the water table and soil vapours of volatile petroleum constituents;
- deeper groundwater containment of various contaminants such as DNAPLs beneath industrial or commercial properties or hazardous waste disposal sites;
- containment around new or existing commercial or industrial sites or landfills where groundwater contamination is likely to occur;
- temporary containment around sites where soil or groundwater contamination is being remediated.

Cutoff walls can serve as one element in a comprehensive program of site restoration that may involve in situ bioremediation, surfactant or steam flushing or other soil or groundwater treatment processes. At a smaller scale, a portion of a contaminated area can be isolated for pilot scale tests of remediation technologies.

Waterloo sealable joint sheet piling provides several unique advantages over conventional walls:

- rapid installation and sealing;
- minimal disturbance of site landscape during construction;
- health and safety problems and disposal costs that arise when contaminated soil is excavated for slurry trench methods are avoided;
- irregular wall shapes are easily constructed;
- can be constructed in built-up urban areas where equipment access limitations would interfere with construction of other types of walls;
- easily built in areas with high water tables, swamps, or surface water bodies;
- convenient use of chemical-resistant sealants;
- less uncertainty in wall performance;
- positive public perception of wall reliability.

These applications and advantages of sealable joint sheet piling indicate that it can be used for controlling a wide variety of environmental problems.

SUMMARY AND FUTURE WORK

The work conducted to date clearly demonstrates that joint sealing effectively reduces leakage through the joints between adjacent sheets of a sheet pile cutoff wall. Leakage can be reduced to such a low value that sheet pile cutoff walls with sealed joints are suitable for a variety of environmental control purposes. These tests were conducted using a field modified prototype sealable sheet piling. Tooling for manufacturing sealable joint sheet piling that does not require field fabrication has been acquired, and production of the first run of Waterloo sealable joint sheet piling is scheduled for October, 1991. Following production, a field test will be undertaken that involves constructing a test cell that extends to a depth of approximately 15 metres. The cell will be hydraulically tested to evaluate its performance. Identifying and evaluating additional materials that may perform well as joint sealants is underway, and is expected to continue through the winter. If there are no unforeseen delays, it is expected that Waterloo sealable joint sheet piling will be on the market by the Spring of 1992.

ACKNOWLEDGEMENTS

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ENHANCED OXIDATION TREATMENT OF CONTAMINANTED WATER USING HIGH POWERED ULTRAVIOLET LAMPS

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ABSTRACT

The **Rayox®** enhanced oxidation process, employing high powered ultraviolet lamps, is a means for the remediation of contaminated water. There is a growing use of enhanced oxidation technologies to address the need to remove small amounts of waterborne contaminants from the environment. Efforts such as Ontario's MISA program have been implemented to regulate the remediation of contaminated water. The **Rayox®** enhanced oxidation process employs high powered ultraviolet lamps in its technology. This project focuses on further developments of the **Rayox®** technology to allow for building more versatile, powerful, efficient systems and thus to allow for the treatment of a wide variety of contaminated waters. In this paper, results are presented highlighting the benefits of the ultraviolet lamps used in the **Rayox®** technology and the resulting treatment of contaminated waters. Results on the lamp and power supply show that the system operates with comparable or better efficiencies than conventional low pressure mercury lamps, thus producing the added benefits of compact design and reduced capital and operating cost. Quartz fouling, a well known problem for this technology, has been addressed by a major development program resulting in an automated quartz cleaning system. Excellent results have been obtained even in the most problematic process waters. Future development efforts will include further improvements in lamp and power supply design and improved process applications to allow for more efficient and powerful cleanup of contaminated water.

INTRODUCTION

The use of enhanced oxidation processes (EOP) to destroy small amounts of hazardous organic compounds present in contaminated groundwater and industrial process wastewater has become increasingly common in the past few years. EOP treatment offers considerable advantages over traditional oxidation methods employing oxidants such as molecular ozone, hydrogen peroxide or hypochlorite due to the participation of the hydroxyl radical (Hoigne and Bader 1976; Peyton et al 1982). The hydroxyl radical (${}^{\bullet}OH$) is a very powerful oxidizing agent that reacts very rapidly with most organic compounds.

Ultraviolet light is employed in EOP primarily for the generation of hydroxyl radicals from the photolysis of hydrogen peroxide (Sundstrom et al 1986; Mansour et al 1984, Borup and Middlebrooks 1987):

$$H_2O_2 \xrightarrow[\text{Light}]{\text{UV}} 2\,{}^{\bullet}OH$$

Once generated, the hydroxyl radical reacts with the organic contaminant in one of two ways: it can add to the contaminant, as is the case for olefins or aromatic compounds, or it can abstract a hydrogen atom to form water, as with alkanes or alcohols. Either of these processes initiates a complex cascade of oxidative reactions leading to mineralization.

Ultraviolet light can also initiate the direct photodegradation of pollutants. Compounds that absorb UV light and have reasonable quantum yields for photodegradation are potential candidates. These would include certain aromatic compounds, chlorinated organics and nitrosodialkylamines.

There have been two types of UV lamps used in enhanced oxidation treatments in the past: low pressure mercury lamps and medium pressure mercury lamps. Low pressure lamps have most of their output centered in a narrow band around 254 nm and operate at low powers, typically 40-120 watts. They have good electrical energy to light energy conversion efficiencies (~30%) but their use in EOP is restricted due to their low power and emission in only a narrow wavelength band. Medium pressure lamps have a broad emission in the ultraviolet range with variable output powers up to around 15 kW. These lamps suffer however from low conversion efficiencies, typically around 10%.

Enhanced oxidation treatment using ultraviolet light has not been fully exploited for the solution of real-world problems due to the following factors:

1. Low power output and narrow bandwidth of low pressure Hg lamps
2. Low efficiencies of medium pressure Hg lamps
3. Potential for fouling of quartz sleeves
4. Application of the same configuration of the treatment process without regard to the nature of the contaminant or its concentration.

The third point is of practical consideration, since it is found in continuous operation that materials such as calcium and iron salts deposit on the quartz sleeves of a water treatment system. These deposits effectively block the UV radiation from reaching the water, thus requiring a costly shut down of the system to clean the quartz.

The **Rayox®** enhanced oxidation system has largely overcome the above deficiencies in the use of ultraviolet light for water treatment. This paper describes work carried out on the investigation of lamp/power supply improvements, automatic quartz cleaning and the effect of additives on pilot and full-scale treatment of contaminated groundwater and industrial process water.

EXPERIMENTAL

Experiments were performed in a batch recirculation set-up. The contaminated water was added to a 30 L, 200 L or 300 L holding tank and was pumped through a reactor housing a Solarchem 1 kW, 4 kW, 6 kW, 10 kW or 30 kW lamp. The volume of water treated varied with the lamp size from 20 L to 300 L. The recirculation flow rate was 20-200 L min^{-1}.

The contaminated water was obtained from actual groundwater or industrial process water sites. The water was used as received without pretreatment. The pH was adjusted as necessary with either sulfuric acid or sodium hyroxide. Samples were withdrawn at regular intervals for analysis. The studies of the quartz cleaning device employed an industrial process water, as well as tap water that was spiked with 700 ppm ferrous sulfate, pentahydrate, 10 ppm sodium carbonate and 30 ppm bentonite. The water was recirculated at 50 L min^{-1} through a **Rayox®** reactor housing a 30 kW lamp.

Samples were analyzed by gas chromatography (GC) or high pressure liquid chromatography (HPLC) as appropriate. GC analysis was carried out on a Varian Model 3300 GC equipped with a flame ionization detector and a 15 m x 0.53 mm i.d. DB-1 column. HPLC analysis were carried out on a Waters Model 6000A pump with variable UV detection and a 15 cm x 0.45 cm i.d. C-18 column.

All reagents were ACS analytical grade and were used without further purification.

RESULTS AND DISCUSSION

Lamp and Power Supply

The basic module of the **Rayox®** enhanced oxidation system is comprised of a stainless steel reactor equipped with a quartz sleeve, an automated quartz cleaning device and a Solarchem lamp and power supply. Hydrogen peroxide or ozone is used as the primary source of hydroxyl radicals. ENOX additives, which are proprietary rate enhancing compounds, may be added to improve the treatment of some pollutants.

For a given application, the cost of an ultraviolet light based technology is dependent on the amount of light required to treat the water effectively. This affects both the capital and operating costs by determining the number of lamps needed and the electrical power consumed by the lamps. To minimize the number of lamps required, we have undertaken a development program focussing on all aspects of the lamp system from the power supply to the delivery of photons to the water.

The photodegradation of pollutants in **Rayox®** usually follows first-order kinetics so different types of lamps can be compared by determining the slope of the first-order plot of the log of the pollutant concentration versus the kilowatt-hours (kWh) of UV energy consumed. The kWh consumed is proportional to incident integrated light intensity, and hence its use allows for the comparison of lamps without the need to perform chemical actinometric experiments that become very difficult for broad band light sources of large power.

The efficiency of the power supply determines the amount of electricity required to power the lamp. Conventional power supplies for medium pressure lamps generally have operated with efficiencies in the 50% range. This is too low a value for practical use as the operating costs become prohibitive. The proprietary Solarchem power supply has been developed over the past 3-4 years and operates with greater than 90% efficiency. There is thus little wastage of power from the mains to the lamp, which results in lower operating costs.

The amount of electrical input energy converted to UV light is taken to define the efficiency of the lamp. The low efficiency of typical medium pressure lamps (~10%) has made them too expensive for commercial environmental applications. An increase in efficiency would make these lamps more competitive, on an operating cost basis, with low pressure lamps which have efficiencies around 30%. In addition, the wavelength range of the light output is particularly important. It is generally found that most organic pollutants absorb UV light more strongly at shorter wavelengths. Figure 1 presents the UV absorption spectra of four common pollutants and it is readily seen that the UV absorption rises dramatically below 250 nm for all compounds. It is advantageous to have significant output below 300 nm and specifically below 250 nm to improve the photodegradation of pollutants. We have compared 4 lamps for their relative abilities to destroy some model pollutants. The lamps compared were an older model Solarchem 1 kW lamp (Solarchem A), an improved model Solarchem 1 kW lamp (Solarchem B), a Hanovia 2 kW medium pressure lamp and a 25 watt low pressure lamp. Experiments were carried out on two test solutions: 100 ppm 1,4-dioxane with 100 ppm hydrogen peroxide or 10 ppm pentachlorophenol (PCP) with 100 ppm hydrogen peroxide. The results are summarized in Table 1 from which the following general conclusions can be drawn:

- The Solarchem A lamp offers 40 - 60% improvement over the Hanovia medium pressure lamp
- The Solarchem B lamp is 30 - 60% better than the Solarchem A lamp
- The Solarchem B lamp operates at efficiencies similar to a low pressure Hg lamp

Table 1

Observed Rate Constants for Treatment with Different Lamps

$$k, \left(\frac{(\text{kWh})}{(1000\ \text{gal})}\right)^{-1} \quad \text{for each lamp}$$

Conditions	Solarchem A	Solarchem B	Hanovia	Low-Pressure
Dioxane/H2O2	0.048	0.078	0.035	0.080
PCP/H2O2	0.125	0.165	0.076	0.175

* **Note**: k is the slope of the line obtained from a plot of log c vs. kWh/1000 gallons US.

These findings are of particular practical importance since it would take 1200 low pressure lamps at 25 watts to equal the photons delivered by one Solarchem 30 kW lamp. The relative space and capital cost of the high power lamp system is more favourable. These results demonstrate the improved operating characteristics of the Solarchem lamps that result in lower capital and operating costs for a treatment system. Evaluation of lamp characteristics as well as further lamp developments are on-going projects under this program.

Quartz Cleaning Device

Once photons are generated from a lamp, it is important to ensure they are transmitted to the water consistently. Water containing dissolved metals or solids can deposit a residue on the quartz sleeve during continuous use. We have developed an automated quartz cleaning device to ensure that the quartz remains clean during continuous use. Tests were carried out on two types of water: an industrial process water and a spiked tap water. The results of the tests have shown that the quartz is kept clean for both types of water. The number of cleaning cycles has been varied between 500 and 30,000 with no deposits observed on the quartz. Figure 2 presents a photograph of cleaned versus uncleaned quartz under similar operating conditions and clearly shows the necessity of a cleaning device. This developmental work is now essentially complete.

ENOX Additives

Solarchem has developed five proprietary additives to which it has given the name "ENOX". These additives speed up the destruction of some pollutants. Figure 3 shows the effect of addition of ENOX 510 on the treatment of benzene, toluene and xylene (BTX) in a contaminated groundwater. The addition of ENOX 510 results in a 3 to 4 fold increase in the rate of destruction of the pollutants. The **Rayox®** process also effectively destroyed the anti-oxidant methyl-t-butyl ether (MTBE). This compound is not amenable to carbon treatment, which has been the standard remediation technique for BTX. Further research is underway on additives for different pollutants.

Treatment Examples

The following examples have been selected to show the type of results that can be obtained with the **Rayox®** system. The results are from laboratory pilot scale work using 1 kW or 6 kW lamps. Residence times in the corresponding full scale systems range from 6 seconds to 3 min for each 90% destruction of pollutant.

N-Nitrosodimethylamine (NDMA)

NDMA absorbs light strongly at 228 nm and photolyses without the need for hydrogen peroxide. Figure 4 shows results obtained on NDMA treatment using photolysis alone. The full scale system offers four orders of magnitude destruction for only $0.40/1000 gallons operating cost.

Chlorinated Organics

A groundwater contaminated with a variety of compounds including chlorinated organics has been tested and the results are presented on Table 2. All compounds, including the more refractory dichloroethane, trichloroethane and chloroform, were treated to below discharge requirements.

Table 2

Treatment of Chlorinated Organic Compounds

Compound	Initial Concentration (ppb)	Final Concentration (ppb)	Discharge Requirement (ppb)
Benzene	296	0.75	5
Toluene	0.81	<0.1	24
Chlorobenzene	6.03	0.22	0.3
1,1-Dichloroethane	1100	1	10
1,1,1-Trichloroethane	640	11	200
Chloroform	223	2.87	350
Trichloroethylene	441	0.17	30
Tetrachloroethylene	41.5	0.01	10

Pentachlorophenol (PCP)

A storm runoff water at a wood treating plant is contaminated with up to 5000 ppb of PCP. Figure 5 presents the results of **Rayox®** treatment of this water demonstrating the successful results obtained.

SUMMARY

This paper has focussed on ultraviolet light application in enhanced oxidation treatment. Results have been presented showing the affect of lamp type on treatment efficiency. The **Rayox®** process has been developed utilizing a high efficiency lamp and power supply, an automated quartz cleaning device and proprietary ENOX additives. These developments result in a powerful system that can treat virtually any organic pollutant to required discharge levels. Further research and development will focus on system improvements in operability and maintainability and process modifications to improve the overall costs of treating contaminated water.

ACKNOWLEDGEMENTS:

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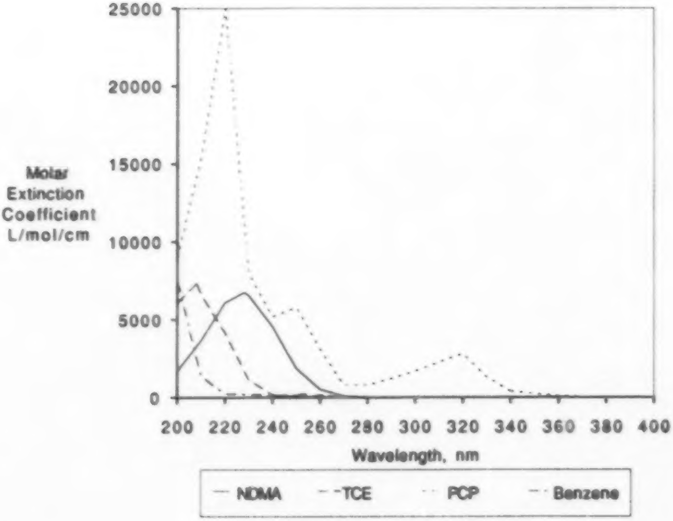
Sundstrom. D.W., H.E. Klei, T.A. Nalette, D.J. Reidy and B.A. Weir (1986), *Hazard. Waste Hazard. Mat.* 3, 101.

FIGURE 1

RELATIVE UV ABSORPTION OF COMMON POLLUTANTS



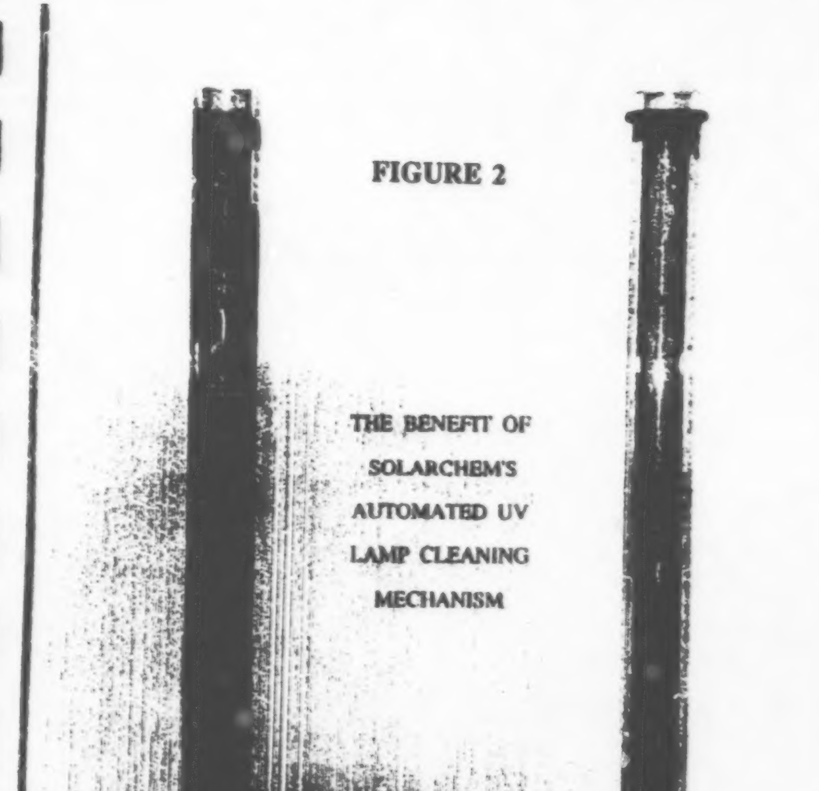


FIGURE 2

THE BENEFIT OF SOLARCHEM'S AUTOMATED UV LAMP CLEANING MECHANISM

FIGURE 3

RAYOX TREATMENT OF GROUNDWATER CONTAMINATED WITH BTX

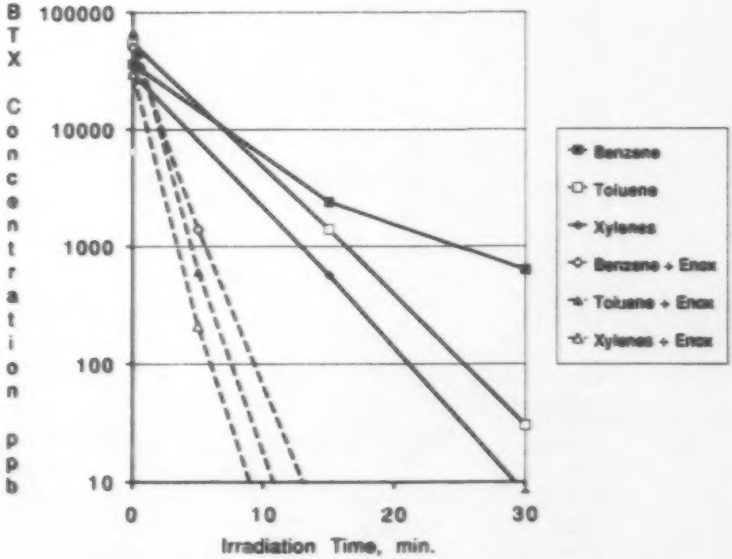


FIGURE 4

RAYOX TREATMENT OF NDMA

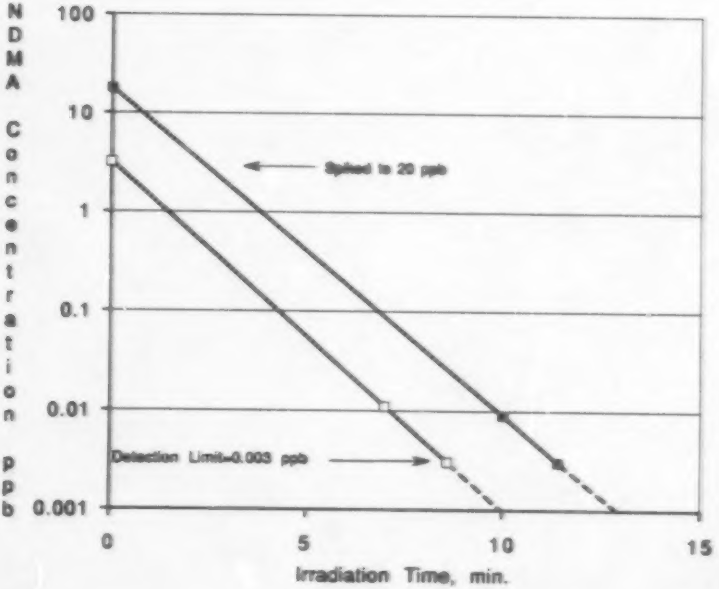
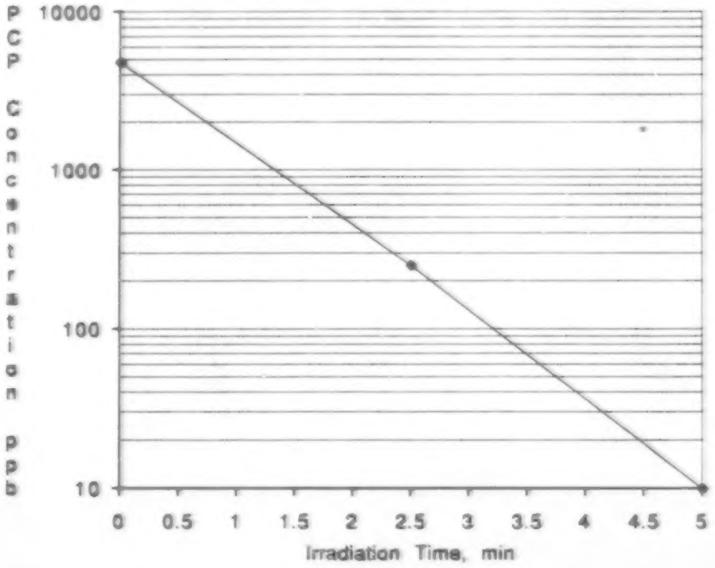


FIGURE 5

RAYOX DESTRUCTION OF PCP
IN STORM RUNOFF WATER



DEINKING OF WASTEPAPER BY HIGH PRESSURE STEAM TREATMENT FOR PAPER REUSE

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ABSTRACT

A novel steam-explosion technology has been investigated for the effective deinking of selected wastepaper and paperboard furnish for recycling. The features of the process include the continuous pulping of wastepapers at high consistency under high temperature (pressure) steam treatment for short duration, followed by explosive decompression. Deinking of selected wastepaper has been studied both at the laboratory and pilot scales. The steam-exploded pulp has been evaluated for cleanliness (visual and image analysis) and physical and optical properties. Numerous potential advantages in the steam-explosion approach to deinking have been demonstrated from the technical trials. The overall enhanced cleanliness of the deinked pulp could likely reduce the requirement for downstream cleaning after pulping. An additional potential important advantage is the use of furnishes not currently deinkable by conventional technology. Work is currently in progress to expand the range of wastepaper and paper-board furnishes which could most benefit from the new technology.

INTRODUCTION

Wastepaper has recently become an increasingly serious environmental concern due to the current landfill problems in North America. Although limited recycling of selected wastepaper has been implemented in some Canadian cities, the programs are primarily restricted only to newsprint. There are also considerable limitations with the current wastepaper deinking process technologies. Due to the overall ineffective deinking at the pulping stage, the conventional process generally requires the use of chemicals during pulping, as well as multi-stage downstream screening, washing, floating and bleaching treatment to produce a marketable product. A conventional deinking plant therefore suffers from high capital and operating costs. Moreover, it is well known that current processes cannot handle many common low grade wastepaper furnishes and associated contaminants. It is therefore important that improved wastepaper deinking processes be investigated.

BACKGROUND ON STEAM-EXPLOSION DEINKING PROCESS:

StakeTech has developed and commercialized a proprietary continuous steam-explosion reactor which is currently the only equipment capable of processing wood and agricultural residues at high steam pressure of up to 450 psig on a continuous basis. The company currently owns 120 patents world-wide on its equipment and process technologies for the conversion of lignocellulosic material to cattlefeed, chemical and high yield pulp (S-pulp). Recently the company has extended its process technology for the deinking of wastepaper for recycling.

The steam-explosion deinking process have several unique features. These are distinct from current repulping technologies which generally involves a batch process at low consistency (5-8%), at low temperature (less than 100 C), for long durations (45-60 minutes) and with high energy and chemical consumptions. Steam-explosion processing, on the other hand, is at high steam temperature (and pressure), typically between 160 C to 230 C (up to 400 psig). Pulping is performed at exceedinly high consistency (50% by weight). The process is also continuous, which enables steady-state pulping at all times, thereby ensuring proper process control and uniform product quality. Termination of the pulping reaction is achieved by "explosion", i.e., the sudden release of material from the operating pressure to atmospheric pressure across a discharge valve.

StakeTech, in collaboration with Chesapeake Corp. and Wisconsin Tissue, has carried out steam-explosion deinking of a variety of selected wastepaper and paperboards.

WASTEPAPER RECYCLING:

Deinking of selected wastepapers had been evaluated initially with laboratory scale steam-explosion reactor at the StakeTech laboratory. The steam-exploded pulps, without further treatment, were made into handsheets and evaluated under standard pulp and paper testing conditions, including yields, brightness, physical strength, fiber classification, and cleanliness (visual and image analysis). The effects of various pulping/deinking chemicals, either singly or in combination, on the steam-explosion deinking process were also examined. Studies to date demonstrated superiority of the steam-explosion deinking as compared to the corresponding laboratory scale conventional deinking with various furnishes. Examples include:

- Coated paper - coated groundwood-free sheets with printing, magazines, brochures, packing plant source
- Office waste - post-consumer colored - file stock, office waste, groundwood-free, sorted
- Groundwood shavings - coated printers coupons, newspaper insert, largely edge trim and low in printings

Numerous advantages were confirmed from these studies. The major ones include:

- reduced pulping time (conventional: 30-60 minutes, as compared to steam-explosion: 1-2 min typically).
- reduced pulping chemicals: data indicated that satisfactory deinking could be achieved with reduced chemicals or even in the complete elimination of pulping chemicals in the steam-explosion process. This is not possible with conventional deinking.
- reduced particle size of contaminants (including ink): the data obtained from image analysis objectively demonstrated a drastic reduction in the size of the dirt particles present in the pulp after the steam-explosion treatment.

Examples:

	Average particle size (sq.mm)	
	Conventional	Steam-explosion
Office Waste:	1.59	0.27
Coated Paper:	0.17	0.06
Groundwood:	0.59	0.21

- enhanced overall cleanliness: this was demonstrated by visual comparisons as well as image analysis (based on the sq. mm. of dirt particles present per sq. ft. of the paper examined). The image analysis is currently considered to be the ultimate test for objectively evaluating deinking effectiveness.

Example:

	Dirt count (sq. mm/sq. ft.)	
	Conventional	Steam-explosion
coated paper:	295.3	1.9
groundwood:	28.0	5.1

- reduced energy (steam and electricity) consumption in the overall deinking plant (including pulping and downstream cleaning): this was confirmed by comparing a proposed steam-explosion deinking plant with conventional plant (the energy consumption of steam-explosion process is about 70% of those of conventional process). This is a result of the processing at high consistency and for short durations, as well as for reduced downstream cleaning requirement.

- reduced rquirement for downstream cleaning, reduced requirement for washing water, and reduced requirement for effluent treatment: these are all logical deductions to the enhanced cleanliness of the resulting pulp obtained from steam-explosion deinking without further treatment.

The laboratory studies were scaled up to pilot testing using StakeTech's commercial size (4 Tonnes per hour) continuous steam-explosion reactor followed by downstream cleaning (if applicable) and paper-making using a pilot paper-machine. The results generally confirmed the scalability of the proposed process and supported the laboratory findings on the potential advantages of the technology.

Overall, results with coated paper suggested that the technolgoy for its recycling might be close to commercialization. Depending on the final paper grades to be determined (based on the market sectors targetted), some of the furnishes tested might require only minor downstream cleaning, such as coarse screening, side-hill screening, and fine screening to become acceptable as a marketable products. The low grade unsorted mixed office waste, on the other hand, might require further technology development. The results on office waste were already demonstrated to be superior to conventional deinking process. With the type of office waste tested, the current technology could mix in about 15% of office waste with other furnish to manufacture an acceptable tissue product. The results from steam-explosion indicated that it might be possible to use higher levels of office waste (50%) in a mixed furnish. With proper downstream cleaning and again depending on the final end-products intended, it is foreseeable that a 100% recycled office waste may be marketable using the new technology.

Preliminary economic evaluations had been performed on the steam-explosion deinking process for mixed office waste in tissue application. The analysis showed considerable economical advantages of the new process when compared to conventional deinking technologies.

WASTEPAPER BOARD RECYCLING:

Steam-explosion was also demonstrated to be applicable to the recycling of old corrugated containers (OCC) and resin-based wet strength OCC. The high-temperature and short-duration treatment followed by explosive decompression was demonstrated to result in excellent fiber dispersion. The stickies (such as plastics) normally present as contaminants of the OCC appeared to be tolerated well with the new technology. The bulk of the resulting plastics after steam-explosion were shown to be of a size that could be readily removed by coarse screening alone prior to paper making.

The process was successfully scaled up in a pilot operation using StakeTech's commercial scale continuous reactor. Paper produced by a pilot paper-machine in the trial was of an exceptional cleanliness, superior to current commercial products manufactured using conventional technology with extensive downstream cleaning, washing and screening stages. The steam-explosion technology was demonstrated to work well even with heavily contaminated OCC (normally a plant reject). Particularly encouraging results were obtained with wet strength OCC, which currently could not be recycled and was known to cause considerable problems as a contaminant in the OCC recycling operation. The steam-explosion process was able to effect proper fiber dispersion for the recycling of 100% wet strength furnish to be achieved, even in the absence of chemicals and under the short treatment time used.

Attempts were made at the pilot scale to use old newsprint (ONP) as a filler in OCC manufacturing. The low cost of ONP as a result of the ONP glut in U.S. (which was forecasted to last well into the next decades) provided considerable economic incentives for the approach. Evaluations are currently progressing to determine the extent of strength reduction that may occur at different ONP substitution levels.

With the new technology, the results to date suggested that a simple overall process could be established for the recycling of OCC and wet strength OCC. A simple process scheme might only have to include the following: a shredder, a conveyor (including weightometer and steam or water injection systems to raise the mositure content of the furnish), a StakeTech's Feeder-Digester, dump chest (for furnish dilution), a coarse pressure screen, and a paper machine.

A preliminary economic evaluation of the process had been carried out on the new technology as pertaining to OCC operations. The analysis clearly demonstrated the economic advantages of the new technology when compared with conventional technology.

FUTURE WORK

Overall, the results to date indicated that the technology might be ready for commercialization with some of the furnishes tested. Work under the current project will emphasis on extending the steam-explosion processing technology to the use of wastepaper and paperboard which are not readily recyclable by conventional deinking technologies. The potential effect of the use of chemicals (including surfactants) during steam-explosion for the specific applications will be evaluated.

PLASMA GASIFICATION
FEASIBILITY STUDY
OF
HOSPITAL SOLID WASTE

Presented to
The Ministry of the Environment
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BACKGROUND

Resorption Canada Limited (RCL) has been actively involved over the past few years in R&D with plasma arc technology, utilizing a specially designed 150KW plasma arc torch in their plasma research facility (PRF) in Gloucester, Ontario. Over the years a wealth of experience and knowledge has been gained in the plasma arc processing of carbonaceous materials, pyroprocessing of ores and concentrates, and in industrial heat applications. A major area of concentration has been gasification, whether for the creation of a usable product gas, for the destruction of a waste material, or for a combination of both. A Plasma Heating System (PHS), when utilized in a reactor vessel with the exclusion of oxygen, can be used very efficiently for the gasification of any carbonaceous material. The resultant pyrolysis provides for virtual complete gasification of all combustibles in the source material, while non combustibles are reduced to a non-hazardous solid residue. Hospital Solid Waste (HSW), with its high carbonaceous content, is such an application, which combines energy production with the destruction of a waste material with minimal environmental pollution. Plasma gasification of HSW is, therefore, a very substantial alternative to current forms of disposal.

The energy and environmental characteristics of the plasma gasification of carbonaceous waste materials were studied over the past four to five years when RCL completed extensive experimentation with Municipal Solid Waste (MSW) through cost sharing agreements with the Ontario Ministries of Energy and Environment, Ontario Hydro and other third party firms; Electric Power Research Institute (EPRI), Arthur Gordon Environmental Evaluators Limited, RSP Environnement Inc. and Centerior Energy.

PROJECT SCOPE AND STATUS

With this experience in plasma processing RCL submitted an unsolicited proposal to the Ontario Ministry of the Environment (MOE) for cost sharing consideration to investigate the plasma gasification of HSW. This proposal was approved for an October 1991 commencement with an expected completion of mid 1992. The project will establish optimum operating parameters and then determine the energy and environmental characteristics at these operating parameters. Facility modifications, as identified through the MSW experimentation, will be effected to further improve the environmental results. The PRF is currently being updated for the commencement of first testing.

THE EXPERIMENTAL PROCEDURE

The RCL PRF is shown in Figure 1. Each experimental run covers a duration of up to eight hours, depending on the requirements of the individual run. HSW is very similar in composition to MSW; therefore, the feeder developed for feeding MSW will also be used for the HSW. The pathological and infectious components of the HSW will be simulated, on the recommendation and approval of the MOE, which will negate the requirement to design and build a special feeder, and permit more accurate ultimate and proximate analyses for subsequent comparison purposes. Steam, or water, can be introduced at varying rates, as required, to provide additional oxygen to react with the free carbon forming additional combustible gaseous products.

System control is very versatile and enables one operator to process varying amounts of material up to the maximum capability of the facility depending on the type of material being processed. The operator has continuous readout of critical operational parameters of the process.

The process temperature, as monitored at the inside wall of the reactor vessel, is approximately 1100 deg C. Once this operating temperature is achieved, HSW is weighed, fed into the vessel and processing commences. The optimum feed rate for the process is determined through a combination of the temperature inside the vessel and the amount of product gas being generated.

Solid residue is permitted to accumulate in the bottom of the reactor vessel and is removed at the end of the experimental run by hydraulically tipping the entire vessel. The solid residue is poured into a bed of silica sand.

The volume of product gas generated is continuously recorded on a Bailey gas meter, and a log of all torch operating parameters is maintained to facilitate full analyses at a later time. The product gas chemical composition is monitored with a Gas Chromatograph to ensure a good cross sectional reading of the product gas quality. The product gas can be combusted in a burner directly from the gasification process, or it can be flared on exit.

Environmental sampling and analyses are independently conducted on the product gas, the products of combustion of the product gas and the solid residue.

PLASMA GASIFICATION CHARACTERISTICS

Energy and environmental characteristics of the plasma gasification process were determined through the previous experimentation with MSW.

The energy characteristics as determined within the RCL PRF and as extrapolated through known process improvements to a 50 to 75 tonne per day commercial size installation are as follows:

	LABORATORY RESULTS	COMMERCIAL SIZE EXTRAPOLATION
Conversion Ratio (Energy Out/In)	1.65:1	4.30:1
Overall Efficiency	56.0%	72.2%
Product Gas/Refuse HV Ratio	0.847	0.868
Product Gas HHV (BTU/SCF)	282.15	282.15 (max)
Dry Refuse/Slag Weight Reduction	5.37:1	5.37:1
Wet Refuse/Slag Weight Reduction	8.93:1	8.93:1
Refuse/Slag Volume Reduction	184:1	184:1
El Energy per Tonne Refuse (KWhrs)	1595	612

Commercial size extrapolation includes known improvements obtainable through the use of a larger size and more efficient plasma arc torch, the use of additional refractory lining in the wall of the reactor vessel and economies of scale for heat losses. Conversion ratio is defined as the energy available in the product gas compared to the electrical energy input to the process which created the product gas. A conversion ratio of 4.3:1, therefore, means that for every BTU of electrical energy input to the process through the plasma arc torch there are 4.3 BTUs of usable energy in the product gas. This ratio does not consider any energy recovery from the sensible heat in the hot product gas, the hot solid residue or the torch cooling water, which account for the majority of the 28% losses.

The heat balance for the process is shown in Figure 2, and the chemical composition of the product gas and the solid residue are shown in Table 1. Representative air emission data for Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs), Chlorophenols (CPs), Chlorobenzenes (CBs), Polychlorinated Biphenyls (PCBs) and

Polychlorinated Aromatic Hydrocarbons (PAHs) are shown in Table 2. Leachate toxicity levels for the solid residue are shown in Table 3.

Where possible, the environmental characteristics tables include comparable statistics from National Incinerator Testing and Evaluation Program (NITEP) reports for the Quebec City (Que) and the Prince Edward Island (PEI) incinerators, along with Ontario regulation 309 and Quebec regulation limits, and the Canadian Council of Ministers of the Environment (CCME) guidelines. The Que and PEI incinerators do not have extensive pollution control equipment; Que has an Electrostatic Precipitator and PEI is a dual stage incinerator. However, these installations were selected by NITEP as having designs which exemplified projected future trends in incinerator technology in Canada and they underwent an extensive optimization/modernization upgrade to a state-of-the-art design immediately prior to testing. In marked contrast, the RCL PRF was not designed with pollution control in mind, rather its design and optimization concentrated only on the gasification process.

The environmental results are self evident, indicating that almost all aspects of the plasma gasification process are superior to the most optimized incineration processes. PAHs are the only emission found to be higher than incineration levels; however, in retrospect this would be expected since PAHs are destroyed in an oxygen rich environment, whereas the plasma gasification process is designed to minimize the amount of oxygen present. In the plasma gasification process PAHs will be destroyed primarily through an efficient combustion of the product gas.

The solid residue from the process is monolithic with toxic element leachability levels, even on fully crushed samples, substantially lower than the Environmental Protection toxicity standards currently in either the Ontario or Quebec regulations. These levels are also significantly lower than the normal levels of toxicity found in the ashes of conventional incineration processes. The results shown in Table 3 are from fully crushed samples, whereas, if these samples had been prepared and analysed in accordance with accepted procedures for a monolithic material, even lower results would have been obtained.

PLASMA GASIFICATION ADVANTAGES/INNOVATIVE FEATURES

The plasma gasification process appears to have substantial cost, size, operability and environmental advantages/innovative features over current disposal methods. These features include:

HEAT SOURCE

a. Independent heat source - provides flexibility since it can be controlled at will and can process material from very little to its maximum capability and still operate at an optimal operating point. This relative ease of controllability makes it particularily amenable to off-peak processing to substantially reduce input electricity charges;

b. Higher processing temperature and heat transfer rate constantly available - conducive to the breakdown of most chemical bonds with the prospects of forming less complex and non-polluting compounds; and

c. Processing temperatures can be varied and maintained - controllable at the will of the operator to meet varying input material composition demands.

PROCESS

a. Very little oxygen (much less than for stoichiometric combustion) present through the process - results in minimal combustion and a richer product gas;

b. Unaffected by variations in moisture content in input material - optimal operation can be maintained;

c. Two distinct processes before exhausting to the atmosphere - distinct separation between the gasification process and the combustion process to minimize problems associated with the direct combustion of the input material;

d. Reaction of the moisture in the input MSW with the free carbon to form additional combustible products - results in the virtual complete removal of carbon from the input material;

e. Effluents/residues can be recirculated - catch material from pollution control equipments, as may be required through different installations, can be reinput into the process to eliminate separate disposal requirements; and

f. No new smokestack required - combustion can be accommodated in existing boilers to negate the requirement for an additional smokestack with its inherent high degree of public rejection.

PRODUCT GAS

a. Flammable gas produced as a discrete product - provides system flexibility. It caters to varying energy demand needs since the product gas can be used immediately, piped elsewhere or stored for later use; and

b. Small volume to be treated by scrubbers - cost and complexity of pollution control equipment is minimized.

PHYSICAL

a. Small size - results in lower capital costs; and

b. Installation versatility - small size enhances integration into existing facility superstructure, and also installation largely underground for noise abatement and to present a more aesthetically pleasing appearance.

SOLID RESIDUE

a. Non-combustibles in the input material, such as glass, metals, dirt, etc., melt and chemically combine into a dense, inert and non-hazardous solid;

b. Immense volume reduction from shredded refuse to slag - would be even greater with as-received;

c. All input objects completely melt and are unrecognizable in the output solid residue;

d. Molten slag acts as a secondary heat transfer medium on the bottom of the vessel;

e. Inert, non-leachable solid residue may have cost effective commercial uses - indications are for use in construction, insulation and packaging industries; and

f. No continued use of landfill - frees up valuable real estate and alleviates continuing liability from leachate toxicity.

DISADVANTAGE

The primary disadvantage of the plasma gassification process is the operating costs associated with the high electrical consumption. This cost is somewhat offset by the higher volume of product gas generated and, in some cases, it can be further alleviated by operation at lower power during peak hydro usage periods. For example, demand charges can be 30%-90% lower, depending on the hydro district, for operation between 8PM and 8AM and all day Saturday and Sunday, which potentially can be used to advantage. Cogeneration could also be very advantageous to offset the hydro operating costs. Initial assessment of cogeneration indicates that the full process could be virtually self sustaining.

CONCLUSION

Historically, environmental standards are invariably made more stringent and improved standards are developed whenever new developments show that they can reliably meet more stringent limits. Plasma gasification shows the potential of being able to set such new standards.

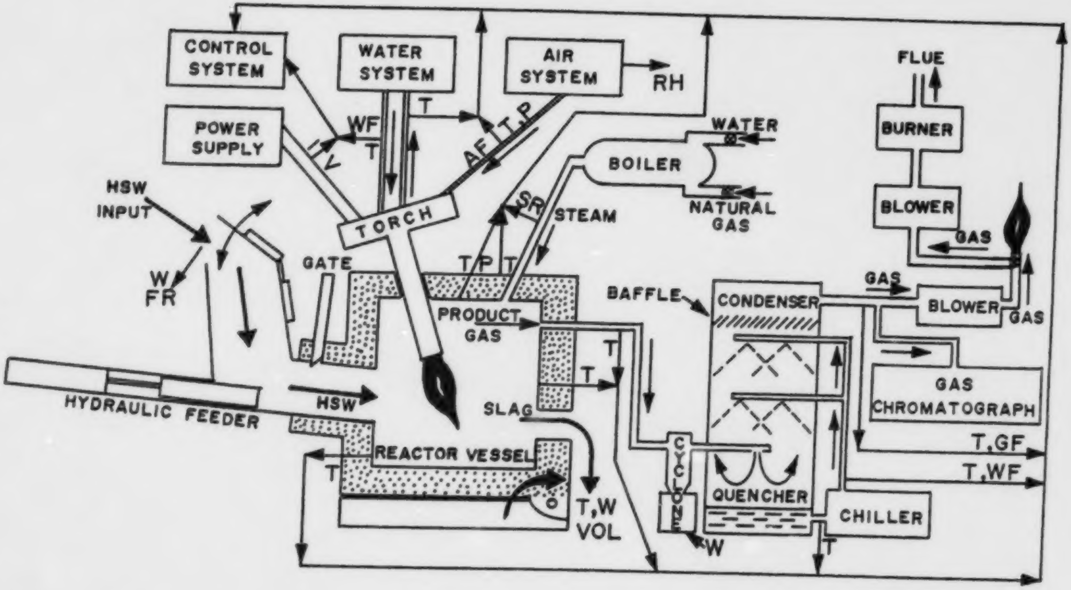
ENCLOSURES

FIGURE 1 - RCL PLASMA RESEARCH FACILITY
FIGURE 2 - MSW COMMERCIAL SYSTEM HEAT BALANCE

TABLE 1 - PRODUCT GAS AND SOLID RESIDUE CHEMICAL COMPOSITION
TABLE 2 - AIR EMISSIONS - PLASMA GASIFICATION OF MSW
TABLE 3 - LEACHATE TOXICITY - PLASMA GASIFICATION OF MSW

RESORPTION CANADA LIMITED

FIGURE I - PLASMA RESEARCH FACILITY


CONTROL SYSTEM
WATER SYSTEM
AIR SYSTEM
RH
POWER SUPPLY
WF
T
I
V
T
AF
T,P
HSW INPUT
W
FR
TORCH
SR
STEAM
BOILER
WATER
NATURAL GAS
FLUE
BURNER
BLOWER
GAS
GATE
T
P
T
BAFFLE
CONDENSER
GAS
BLOWER
GAS
PRODUCT GAS
T
T
GAS CHROMATOGRAPH
HYDRAULIC FEEDER
HSW
SLAG
REACTOR VESSEL
T
T,W
VOL
CYCLONE
W
QUENCHER
CHILLER
T
T,GF
T,WF

I—CURRENT (AMPS)
V—VOLTAGE (VOLTS)
T—TEMPERATURE (DEGREES C)
GF—GAS FLOW (SCFM)
P—PRESSURE (PSIG)
W—WEIGHT (LBS)
RH—RELATIVE HUMIDITY (%)
WF—WATER FLOW (GPM)
FR—FEED RATE (LBS/HR)
SR—STEAM RATE (LBS/HR)
AF—AIR FLOW (CFM)
VOL—VOLUME (CF)

RESORPTION CANADA LIMITED

MUNICIPAL SOLID WASTE YIELDS

FIGURE 2: COMMERCIAL SYSTEM HEAT BALANCE
(FROM R&D RESULTS FEBRUARY 1988)

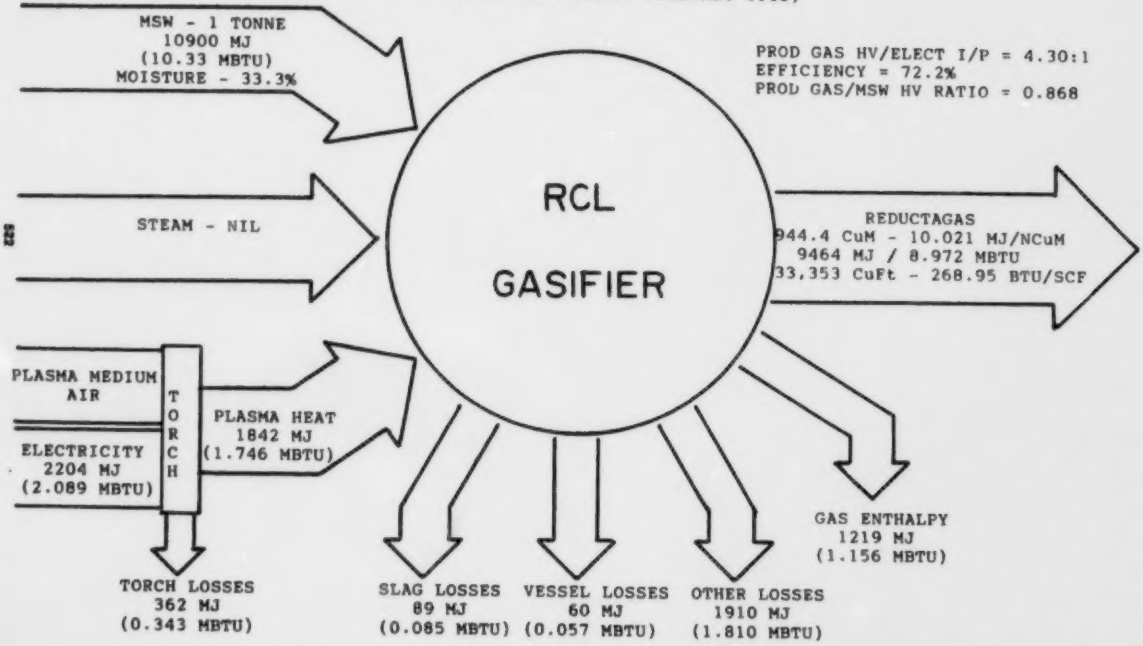

MSW - 1 TONNE
10900 MJ
(10.33 MBTU)
MOISTURE - 33.3%
STEAM - NIL
PLASMA MEDIUM
AIR
ELECTRICITY
2204 MJ
(2.089 MBTU)
TORCH
PLASMA HEAT
1842 MJ
(1.746 MBTU)
TORCH LOSSES
362 MJ
(0.343 MBTU)
RCL
GASIFIER
PROD GAS HV/ELECT I/P = 4.30:1
EFFICIENCY = 72.2%
PROD GAS/MSW HV RATIO = 0.868
REDUCTAGAS
944.4 CuM - 10.021 MJ/NCuM
9464 MJ / 8.972 MBTU
33,353 CuFt - 268.95 BTU/SCF
SLAG LOSSES
89 MJ
(0.085 MBTU)
VESSEL LOSSES
60 MJ
(0.057 MBTU)
OTHER LOSSES
1910 MJ
(1.810 MBTU)
GAS ENTHALPY
1219 MJ
(1.156 MBTU)

TABLE 1: PRODUCT GAS & SOLID RESIDUE CHEMICAL COMPOSITION

PRODUCT GAS COMPOSITION - (at max heating value)

HYDROGEN	41.2%
CARBON MONOXIDE	29.7%
NITROGEN	17.0%
CARBON DIOXIDE	8.3%
METHANE	3.2%
OXYGEN	0.3%
ACETELYNE	0.2%
ETHYLENE	0.1%

SOLID RESIDUE COMPOSITION - (major elements only)

ELEMENT	ELEMENT PERCENT	OXIDE PERCENT
ALUMINUM	9.5	18.0
CALCIUM	10.4	14.6
IRON	2.3	3.3
MANGANESE	0.1	0.2
PHOSPHORUS	0.4	0.8
POTASSIUM	1.6	1.9
SILICON	23.2	49.7
SODIUM	3.8	5.1
TITANIUM	0.6	1.1
TOTAL	51.9	94.7

TABLE 2: AIR EMISSIONS - PLASMA GASIFICATION OF MSW
(CONCENTRATIONS PER NORMAL CUBIC METER)

COMPOUND	RCL LAB RESULTS	EXISTING INCINERATOR(1)	CCME GUIDELINES
SEMI-VOLATILE ORGANICS			
TOXIC EQUIVALENCY			
DIOXINS (NANOGRAMS (NG))	0		
FURANS (NG)	0 - 0.5		
TOTAL	0 - 0.5		0.5
ACTUAL VALUES			
DIOXINS (NG)	ND	19 - 298(A)	
FURANS (NG)	3 - 10	44 - 306	
CHLOROPHENYLS (MICROGRAMS (UG))	ND	5 - 24	
CHLOROBENZENES (UG)	0.6 - 3	3 - 10	
POLYCHLORINATED BIPHENYLS (UG)	ND	2 - 7	
POLYAROMATIC HYDROCARBONS (UG)	1900 - 15000	4 - 22	

(1)(A) - EXISTING INCINERATOR AT QUEBEC CITY - NITEP REPORT EPS 3/UP/5

TABLE 2: AIR EMISSIONS (CONTINUED)
(CONCENTRATIONS PER NORMAL CUBIC METER)

COMPOUND	RCL LAB RESULTS	EXISTING INCINERATOR(1)	CCME GUIDELINES
METALS			
ANTIMONY (MILLIGRAMS (MG))	0.02 - 0.05	0.5 - 2.6(B)	
CADMIUM (MG)	0.004 - 0.03	0.6 - 0.9	
CHROMIUM (MG)	0.02 - 0.08	0.03 - 0.1	
LEAD (MG)	0.2 - 0.6	8.4 - 15	
MERCURY (MG)	ND	0.5 - 0.9	
NICKEL (MG)	0.02 - 0.08	0.2 - 0.5	
ACID GASES			
HYDROGEN CHLORIDE (MG)	0.1 - 0.6		75
HYDROGEN FLUORIDE (MG)	0.07 - 0.7		
HYDROGEN BROMIDE (MG)	ND		
NITROGEN OXIDE (PPM)	158 - 305	169 - 246(A)	
SULPHUR DIOXIDE (PPM)	66 - 69	128 - 225	
PARTICULATES			
MG PER NORMAL CUBIC METER	2.4 - 9.9	167 - 247(B)	20

(1)(A) - EXISTING INCINERATOR AT QUEBEC CITY - NITEP REPORT EPS 3/UP/5
(B) - EXISTING INCINERATOR AT PRINCE EDWARD ISLAND - NITEP REPORT EPS 3/UP/1

Table 3: LEACHATE TOXICITY - PLASMA GASIFICATION OF MSW
(MILLIGRAMS PER LITRE - CRUSHED SAMPLE)

ELEMENT	RCL LAB RESULTS	ONTARIO REGULATION	QUEBEC REGULATION
ALUMINUM	0.03 - 0.18		
ANTIMONY	ND - 0.006		
ARSENIC	ND	5.0	
BARIUM	0.03 - 0.1	100.0	
BERYLLIUM	ND		
BISMUTH	ND		
BORON	ND	500.0	
CADMIUM	ND	0.5	0.1
CALCIUM	1.15 - 3.3		
CHROMIUM	ND	5.0	0.5
COBALT	ND		
COPPER	0.07 - 0.09		1.0
IRON	0.57 - 1.79		17.0
LEAD	0.01 - 0.02	5.0	0.1
LITHIUM	ND		
MAGNESIUM	0.15 - 0.2		
MANGANESE	0.01 - 0.02		
MERCURY	ND	0.1	0.001
MOLYBDENUM	ND		
NICKEL	0.005 - 0.01		1.0
PHOSPHORUS	ND		
POTASSIUM	0.05 - 0.1		
SELENIUM	ND	1.0	
SILICA	0.68 - 1.16		
SILVER	ND	5.0	
SODIUM	0.1 - 1.3		
STRONTIUM	ND		
TELLURIUM	ND		
TIN	ND		
TITANIUM	ND		
VANADIUM	ND - 0.015		
ZINC	0.02 - 0.05		1.0

ND - NOT DETECTED

VOLUME II

SESSION E

ENVIRONMENTAL TECHNOLOGIES PROGRAM

POSTER PRESENTATIONS

DEVELOPMENT OF MEMBRANE TECHNOLOGY FOR DRINKING WATER PRODUCTION: TREATMENT OF COLOURED WATER

C. Smith* and A. Deutschmann, Zenon Environmental Inc., Burlington, Ontario, L7N 3P3

Some drinking water supplies, particularly those in the northern part of Ontario, are highly coloured. Although this may not represent a direct threat to the health of consumers, these substances contribute to the formation of trihalomethanes when the water supply is chlorinated. Conventional water treatment technologies using coagulation and sedimentation followed by filtration do not effectively remove these compounds, and concern over potential health effects has resulted in increasingly stringent government limitations for trihalomethane content in treated waters.

Membrane technology offers one promising solution to this problem. Although membranes are not yet commonly used in municipal water treatment, ultrafiltration and nanofiltration are emerging technologies which offer significant potential as effective processes for removal of particles and higher molecular weight organic compounds. Nanofiltration has recently been successfully applied for treatment of coloured groundwater supplies in Florida, and application for coloured surface supplies is currently of interest. Intensive research efforts are being directed at developing membrane processes to a commercial stage for application in potable water treatment

This study was undertaken to determine the technical and economic feasibility of membrane nanofiltration technology for the removal of colour and trihalomethane precursors from drinking water sources. In-house testing of the performance of several commercially available membranes in parallel with near commercial membranes developed by Zenon will be performed on three different water supplies. Two membranes will then be selected for on-site pilot testing at one of the test sites.

In-house baseline tests using a synthetically prepared water source with colour levels up to 200 APHA have recently been completed, and testing on the first natural water supply is underway. The first test site is a small community in northern Ontario drawing from a surface supply where colour levels range from 40 to 150 APHA.

Pilot testing is expected to take place in early 1992, and results will be used to develop a proposed plant design. The process will be evaluated against conventional treatment and a complete technical and economic assessment will be carried out. The potential for commercialization and market estimates will be also be assessed.

EP2

Expert System Software Development for Assessment of Solid Wastes Leaching and Disposal - 'LANDIS' Expert System

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Abstract

LANDIS (LANd DISposal) is an expert system based software decision tool. Its purpose is to guide the user through a solid waste assessment process to determine the suitability of disposing a specific waste in a specific landfill site. Expert system rules control the evaluation process and incorporate the expertise necessary to render final conclusions and recommendations from the evidence gathered during a LANDIS consultation.

The LANDIS program consists of several interactive modules under the control of the expert system rules and knowledge base:

- relational database management system for storage, retrieval and analysis of waste physical/chemical characteristics
- HELP landfill design and hydrological model with a separately-designed graphical control interface (Hydrological Evaluation of Landfill Performance, ver. 2.05, USAE Waterways Experiment Station, Vicksburg, MS; widely-used and validated with full scale sites)
- location/climate database management system for maintaining and adding climate data to the HELP model (eg. Canadian sites)
- consultation user-interface system

The primary types of information requested and generated during a consultation are:

- waste physical and chemical characteristics,
- waste leaching characteristics,
- target landfill design, local climatic factors and landfill hydrology,
- controlling leaching mechanism,
- concentration and mass flux of contaminant(s) leaving the landfill projected over time (inorganic species only can be determined at this time).

LANDIS has been designed from the outset to be applicable to regulatory solid waste assessments. Current regulatory practice utilizes the results of physical/chemical characterization and one or more bench-scale leaching protocols (protocol types are specific to each provincial jurisdiction) to determine whether a solid waste is suitable for land disposal. LANDIS provides a logical extension to this practice by *incorporating the characteristics of the target landfill site* while utilizing the standard procedures and protocols to determine waste characteristics. In addition, LANDIS utilizes a battery of leaching protocol types in conjunction with waste

properties and target landfill hydrology to determine the controlling leaching mechanism and apply the leaching protocol test procedures most suited to this leaching mechanism. With this information, the concentration and mass flux of the contaminants of interest leaving the landfill over time (source terms) can be calculated and projected in the future. The suitability of disposal of a specific waste in a specific landfill is determined, therefore, by the concentration or mass loading of specific contaminant species projected over time. The methods used are a combination of standard laboratory testing protocols and the fully-validated HELP landfill hydrological model.

LANDIS is also a very useful tool for conducting 'what if' hypothetical scenarios. This capability can be employed for purposes of design or to screen waste and/or landfill disposal options (eg. waste solidification/stabilization options, effect of capping landfill, liner properties, etc.). Waste characterization/leaching data, either from individual waste entries or as generic waste type properties, can be utilized in a screening consultation run. Consultations can be interrupted and re-started at the same point at a later time. Thus, multiple consultations can be run simultaneously.

LANDIS is normally operated as an integrated multi-module application. However, the waste characteristics/leaching database and HELP model (with graphical interface) can also be run as independent programs. The database system is, in itself, a valuable resource which can be used to study and analyze leaching data using built-in statistical tables and a query-based report generator. The original HELP model character-based interface has been upgraded to a 'Windows-like' graphical interface which greatly enhances its usability while preserving its computational core.

The full integrated program will run on a IBM PC-AT compatible computer equipped with a VGA graphics card/monitor, math co-processor and hard disk (386/486 CPU recommended). A fully functional prototype has been developed along with technical documentation, a user guide, and tutorial. LANDIS is intended for use by regulatory agencies or other users who have an understanding of solid waste leaching and familiarity with laboratory bench-scale leaching protocols. The program has not been designed for a novice user.

This project is jointly funded by the Environmental Technologies Program of Environment Ontario, the Canadian Electrical Association and Dearborn Chemical Co. Ltd. Over the next two years the program will be expanded to include a wider variety of waste types and more information specific to Canadian climate and cold weather effects, such as frost penetration, to be included in the HELP model. System validation will then be conducted based on a review of the knowledge base by domain experts and one or more full-scale site waste disposal assessments. A commercial version of the program and documentation will then be released.

CONVERTING SEWAGE SLUDGE INTO LIQUID HYDROCARBON

THE "OFS PROCESS"

D. Martinoli, SNC Inc., Oakville, Ontario

In 1982, Environment Canada, through its Wastewater Technology Centre in Burlington, Ontario, undertook to verify the conversion of wastewater treatment sludge into liquid hydrocarbon.

The principle of low temperature gasification of sewage sludge to produce fuels has been known for several year. France issued a patent to Saburo Shibata entitled "Procédé de fabrication d'une huile combustible à partir de boue digérée" in November 1938. However, in 1982, two German scientists from the University of Tübingen in Germany demonstrated the mechanism by which the sludge is converted into oil.

They heated dried sludge to 350°C in an oxygen-free environment for approximately 30 minutes producing oil, char, gas and water. Oil yields ranged from 18% to 27%, and char yields from 50% to 60%. The oil had a calorific value of approximately 39 MJ/kg, and the char, approximately 15 MJ/kg.

Environment Canada preliminary bench-scale experiments validated the previous results. A large technology demonstration and development program led to the design and construction of two 1 t/day pilot plants. The first one was built in 1986 in Hamilton, Ontario, and the second one in 1988 in Perth, Australia. These two pilot-scale plants have a capacity of 40kg/h each, which is equivalent to 1 t/day of dry sludge.

The bench-scale reactor has been used to evaluate process performance and to obtain data on a number of sludges. This reactor, which is 5 cm in diameter and 100 cm long is made up of two zones, the first for volatilization and the second for conversion. WTC has operated the system using over 25 different sludges from Canada, the United States, Australia and the United Kingdom.

Based on the results of the bench-scale reactor tests, Environment Canada contracted with a subsidiary of SNC in 1985 to design, construct and operate the first pilot plant to confirm the bench-scale results and the projected energy savings. This 1 t/day pilot plant, includes a 1 m^3 sludge storage bin, a sludge feed system, a 25 cm diameter by 3,5 m long reactor, a char discharge system, a direct-contact condenser, an oil-water separator, and a propane burner to heat the reactor. It is similar to the bench-scale reactor described above, except for the method of heating the reactor.

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In September 1986, this unit was delivered to the Woodward Avenue Sewage Treatment Plant in the Hamilton-Wentworth Regional Municipality and has since been operated with three different sludges, namely the raw sludge from Atlanta, and digested sludges from Rockford and Hamilton.

A second generation pilot-scale reactor was built in Perth, Australia in 1988. Originally, this unit was located at the Subiaco Wastewater Treatment Plant of the Water Authority of Western Australia (WAWA) in Perth in Western Australia. This unit was moved to Sydney and was used to test the sludge from the Malabar Wastewater Treatment Plant.

The object of the testing program was to collect all the process data necessary to design a full-scale demonstration plant. The tests were also used to evaluate any environmental impacts. The results of the test program have been analyzed and found well within the requirements of existing regulations.

The tests were carried out on both raw and digested wastewater sludge. As expected, the oil yields from raw sludge are generally greater than from digested sludge, because in the sludge digestion process, volatile materials are destroyed and not converted into oil. The oil yields go from a high of 46% for raw sludge to a low of 13% for digested sludge, and are a function of the reactor's operating temperature and the source of the sludge. Oil viscosity is lower for digested sludge than for raw sludge. It has also been observed that viscosity decreases with increasing temperature, but no definite relationship has yet been identified between operating temperature and the oil's calorific value.

Fine tuning continues in the Canadian and Australian pilot plants, and some modifications have been made to improve operation and performance. The results from these two plants, which have been operated with different sludges, have generally confirmed that:

- The system is capable of converting the sludge and producing usable car.
- The heat distribution on the reactor shell supplies a conversion temperature which allows the relatively low solids retention times.
- Throughput capacity of 40kg/hour can be reached.
- The oil, reaction water and NCG can be separated.
- The performance is similar to that of the bench-scale reactor.

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Conceptually, an OFS plant includes, in addition to the OFS reactor, 3 processes that have been used and proven in sludge management systems:

- Dewatering, to produce a sludge cake of 30% or more dry solids.
- Drying, to bring the sludge to 95% or more dry solids.
- Energy generation, to convert the char, the non-condensable gases (NCG) and the reaction water into thermal energy.

The OFS process has the following advantages:

- Energy considerations - The OFS system is expected to be an extremely energy efficient option. This is due to several factors such as thermal drying and the conversion into oil by a chemical process with an efficiency greater than 90%, rather than by a biological or thermal process. Consequently, this system is a net energy producer and approximately 50% of the sludge's gross energy is recovered in the form of hydrocarbon. Equally important is that it is the only system to produce a liquid hydrocarbon, easy to store and transport, and essential for several industries in the petroleum sector as special additives.
- Design and operating flexibility - The OFS process requires less space, thus a smaller building and a reduction in the capital cost combined with a reduction in the operating costs such as heating, electrical maintenance, etc. Because an OFS plant includes a number of independent sludge processing units, plant expansions and retrofits are much easier and less costly.
- Environmental superiority - The OFS system provides complete pathogen destruction, odor control, metal immobilization and air pollution reduction.
    - Viruses and bacteria are completely destroyed in the three consecutive thermal processes, namely drying (30-90°), conversion (450°C for more than 30 minutes) and combustion in the fluid-bed furnace (900°C).
    - Odor control in an OFS plant is facilitated by the fact that each step of the process is totally enclosed and that the air from the process is used as combustion air for the fluid-bed furnace.

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- The fate of the heavy metals in the OFS process has been well defined. The numerous laboratory and pilot plant data indicate that the heavy metals, with the exception of mercury, are found in the char of the system. In the combustion of the char, the heavy metals are retained in the ash and are converted into non-leachable oxides and silicates.

- A significant feature of the OFS process, as compared to incineration, is that the fluid-bed furnace is fed by dry fuels rather than by wet sludge. The quantity of exhaust gas generated by the fluid bed, and the need for air pollution control equipment are thus greatly reduced. The fluid-bed furnace is in fact known for its very high environmental and energy efficiency. In addition, its hot flue gases are used to dry the sludge.

- Cost effectiveness - With the revenues from hydrocarbon sales, and the fine tuning of the system which will lead to a decrease in construction costs, we can expect a short-term objective of $250/ton for dry sludge treated with the OFS process.

Enersludge inc., a Canadian company 50% - owned by SNC inc. of Montreal, and 50% - owned by Campbell Environmental limited (CEL) of Perth, Australia, signed an exclusive license agreement with Canadian Patents and Development limited. Following this agreement, SNC began marketing and carrying out OFS projects in North America, while CEL covered Australia and the southeast Asian countries (Pacific Rim).

Currently, three projects are at various stages of development:

1. **The Municipality of Metropolitan Toronto**, a 48 tpd capacity plant for Highland Creek Treatment Plant in Scarborough, Ontario.

2. **The Halifax Harbour Cleanup inc.**, a 20 tpd capacity plant for the combined Halifax-Dartmouth wastewater treatment complex which is under design.

3. **The Sydney Wastewater Board**, for the Malabar Treatment Plant in Sydney, Australia, to eliminate ocean dumping.

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EP4

USE OF CHEMILUMINESCENCE TECHNIQUES IN PORTABLE, LIGHTWEIGHT, HIGHLY SENSITIVE INSTRUMENTS FOR MEASURING PAN, NO_2, NOx, AND O_3.

*J.W. Drummond, L.A. Topham, G.I. Mackay, and H.I. Schiff. Unisearch Associates Inc. 222 Snidercroft Road, Concord, Ontario Canada L4K 1B5

Small battery powered instruments for the sensitive detection of nitrogen dioxide (NO_2), and ozone (O_3) will be described. Because of their portability, they are ideal for studies of indoor air quality, measurements from aircraft, and other mobile platforms where power may be limited. For example, a miniature balloon borne sonde, based on the chemiluminescence between luminol and NO_2 has recently demonstrated the ability to measure ambient mixing ratios of NO_2 between ground level and an altitude of 33 km. A converter to enable measurements of NOx by the Luminox^R NO_2 analyzer is presented. The model LOZ-4 ozone monitor will be described. Ozone is measured by using its chemiluminescence with the dye Eosin Y. In comparison with ehtylene based ozone detectors, the LOZ-4 has beeter sensitivity, and does not require a troublesome and flammable gas. The O_3 measurement is virtually interference free. In contrast, the widely used photometric O_3 measurement technique has demonstrated significant interferences in polluted air (presumably due to organic compounds that absorb light at the 253.7 nm wavelength). Finally, a sensitive instrument for measuring PAN will be described. It uses a gas chromatograph to separate the PAN from the whole air sample before detection by Luminox^R techniques. Field measurements for all species are presented.

ENVIRONMENTALLY RATIONAL SOLUTIONS: GOOD BUSINESS DECISIONS WITH POSITIVE ENVIRONMENTALLY IMPACT.

A.A. Wakeford, Administrator,
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A team of three experienced men; an ink technician, a printer and a businessman from Owen Sound, a beautiful tourist area decided to leave a legacy of cleaner land and water to the next generation through the development of ink recycling for large printers. By mortgaging their residences and with the support of a 3 R's grant they have designed, tested, modified and placed in production a mobile ink recycling system.

Year I consists of recycling a single type of printer's ink; coldset black. Emphasis was placed on meeting 'virgin' specifications of Tack, Grit, Grind, Viscosity and Shade. Testing was done and after one year a successful unit was created. Commercialization has paralleled this creation, fighting at all times the perception that 'recycled' is 'inferior'. The sleeping giants, the ink companies, do take some exception to this intrusion into their territory.

Year II introduced the expansion into recycling of all four colours of heatset inks. Currently we are expanding into other ink types, such as sheet fed waterbase and forms ink. Paralleling our technical expansion is our commercial expansion into Quebec and the United States.

Our objective remains a cleaner environment without sacraficing industry's bottom line. Both objectives are possible with rational environmental decisions to recycle and reuse our urban resources.

VOLUME II

SESSION F

PREVENTION, TREATMENT AND REMEDIATION

VERBAL PRESENTATIONS

F1

FROM WASTE TO SECONDARY RESOURCE

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ABSTRACT

The lack of quality control is the first problem we usually encounter in our efforts in the re-cycle or re-use of waste materials generated by manufacturing industry. The variations in properties of wastes are often due to lack of attention in the process in which they are produced and due to contaminations inside the plant.

As secondary resource, it must meet certain requirements including consistency so that its user would have an efficient operation.

The requirements in the current market of a secondary resource must be brought to the attention of waste generator for potential modification of the manufacturing operation to re-classify the waste as a product with due respect. Communications concerning feasible changes in manufacturing progress on one hand and possible financial rewards in the market of secondary resources on the other are essential in converting wastes to secondary resources. As an example, the situation in the re-use of slags from metals industry will be discussed.

1. INTRODUCTION

In order to facilitate our discussion the definition of waste and secondary resources must be clarified. Let us start with an example of a primary resource. In Northern Ontario we have deposits of taconite, a mineral containing about 30% iron, of several billion tonnes. In the 1940's these rocks were of no particular economic value. Due to the development of new processes in mineral dressing, in the 1950's we had several billion tonnes of taconite iron ore, three mines were in operation from the 1960's to 1980's. The great increase on land transportation caused all three Ontario mines to close in the late 1980's, therefore, several billion tonnes of taconite has changed from iron ore to rock again. It is clear that our available technology and market place determines the economic value of particular resources.

The waste in this presentation is industrial waste which is produced in a manufacturing process. It has a negative price at the plant gate of its generator.

A secondary resource is a by-product of a manufacturing process. It has a positive price at the plant gate of its generator.

It must be clearly stated that changes in the market place and technology may convert waste to secondary resource as well as from secondary resource to waste.

2. CHARACTERISTICS OF WASTES

The most important characteristic of waste is that it appears to be useless in the present form. The second important feature is that you and/or your government want to have it removed from your property.

It is no fun and down right unpleasant to examine one's own garbage, we don't know and don't want to know our garbage any better. We just want the garbage men to take these bags away, period! We can imagine that executives in companies do not like their industrial waste any more than we do our domestic equivalent. The first problem we encounter on the way to overcoming the "uselessness" of waste, is the lack of knowledge regarding the properties of waste. In our homes, we put all kinds of wastes in one bag (before the Blue Box Program). In industry, there is no reason, at least in the past, not to put many kinds of wastes together to result in a very large variation of properties. To initiate the equivalent of the Blue Box Program in large manufacturing companies, certainly is the first step in solving the waste problem.

When we try to market our waste as secondary resource, bearing in mind that we must be very specific about the quality of our product.

3. QUALIFICATIONS OF A SECONDARY RESOURCE

In a modern day society and competitive market, no business could survive without an efficient operation and a good product. The company which uses the secondary resource (which was a waste) to substitute for part of their usual raw materials, is no exception. A secondary resource must meet the specifications including consistency as demanded by the user, otherwise, it will become industrial waste soon after its rejection from the market.

4. THE STEEL INDUSTRY AND DOWN STREAM CONTRACTORS

As an example, the description of waste materials in the steel industry is greatly simplified for our discussion. In ironmaking and steelmaking operations, waste oxides produced may be classified into the following three categories:

(a) Waste: steelmaking dust

(b) Secondary Resource: pelletized blast furnace slag

(c) Waste/Secondary Resource: steelmaking slag and ironmaking dust

These waste oxides are usually handled and processed for their disposal or as secondary resources by contractors in the steel plants. Ironmakers and steelmakers are very busy ensuring that their production, the cost and the quality of iron and steel are on targets, has no practice or need up to the present time, to look into their garbage cans. And they don't!

5. FROM WASTE TO SECONDARY RESOURCE

The case of steelmaking dust will be discussed as an example. At steelmaking temperatures of 1600°C, volatile heavy metals which are originated in the recycled steel scrap, vaporize and subsequently are oxidized and collected as dust for air quality control. The major components of dust are iron oxides, zinc oxide, lead oxide and calcium oxide.

The contents of zinc and lead oxides, ranging from 1% to 30% Wt., is a measure of the severity of the problem at hand as well as the potential of converting the dust to secondary resource. At landfill sites, zinc and lead may be leached by rainwater, leading to further contamination of the environment. On the other hand, if the zinc and lead content in dust is high enough and technology is efficient enough to extract these metals from the dust instead of ore, dust becomes a secondary resource.

Many new processes for treating steelmaking dust to produce iron and zinc-lead alloys or zinc and lead oxides have reached pilot plant stage and a very few at the commercial scale of operation. However, their economic viability is yet to be established. The conversion of steelmaking dust to secondary resource will accelerate once either the cost of treating dust goes down due to a technological break-through, or the cost of its disposal goes up due to a shortage of landfill space or other reasons.

6. FROM SECONDARY RESOURCE TO WASTE

In the Hamilton area, the annual production of steelmaking slag is about 800,000 tonnes. Most of it is being used as aggregate for asphaltic concrete for road pavement. The contractors handle slag from the liquid state to crushing, sizing and finally marketing to the construction industry.

Steelmaking slag is chemically unstable and can only be used as aggregate in asphaltic concrete. It has excellent properties for road surface, except it may expand due to hydration resulting in cracking of the pavement. For some reason, this problem becomes more pronounced recently. If this problem can not be solved soon, we will witness the conversion of 800,000 tonnes of secondary resource to waste.

7. EFFORTS SHOULD BE MADE COLLECTIVELY

In our efforts to convert waste to secondary resource or upgrade the secondary resource to a higher priced product (as in the case of ironmaking slag), we are talking of two types of activities:

(i) Technical development of new products based on given or slightly modified raw materials (i.e., wastes). It may involve physical and chemical processing.

(ii) Marketing new products (secondary resources) to old or new customers.

Future success, in our opinion, depends largely on our collective efforts to overcome the following two difficulties:

(i) The lack of technical capability in this problematic area to define the nature of the problem.

(ii) The lack of communication through the chain of companies from the generator of waste to the processor to the user of secondary resources.

PROJECT No. 502G

BIOCONVERSION OF THE MECHANICALLY SEPARABLE PAPER FRACTION OF MUNICIPAL SOLID WASTE TO FUEL ETHANOL

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Ontario Ministry of the Environment
Technology Transfer Conference
Toronto November 25 and 26, 1991

OBJECTIVE

The objective of this research is to reduce the volume of municipal solid waste (MSW) now going to landfill. About half of MSW is paper and paper products such as home and office papers, paperboard packaging and the like. Our results predict that MSW volume will be reduced to about half by diverting or separating MSW paper and processing it to marketable products, thereby doubling the life of landfill sites. The process to be employed is the bioconversion of the paper to the environmentally-friendly, non-petroleum high octane motor fuel ethanol. During this past year, we have found that enzyme liquefaction of waste paper and fermentation of the resulting sugars has given high yields, 350 - 400 liters per tonne, at a concentration high enough for efficient distillation. This translates to 200 liters per tonne MSW. There is enough waste paper in Ontario's garbage to displace 10% of Ontario motorists' useage of gasoline, all now based on imported oil. In a parallel project we have found an efficient method of making the main cellulase enzyme, to be used for saccharification of the MSW-paper at an acceptable cost.

This research has an industrial orientation, to encourage industry to apply our findings. The first stage of our development plan is based on waste paper from industrial and commercial sources, of which there is enough available in the Toronto Area and other urban centers in Ontario. Our high yields of ethanol are obtained by a simple process: enzymatic saccharification, fermentation, distillation and dehydration. We plan to make our own enzymes on site, and to ferment with ordinary bakers' yeast.

INDUSTRIAL DEVELOPMENT

Our industrial development plan begins in Metro. Our technology is sufficiently advanced that we are now working to arrange financing for our first plant. We intend to purchase the St. Lawrence Starch ethanol distillery in Port Credit, which recently shut down. It is an excellent fermentation, distillation and dehydration plant for our intended products. We plan a 6 month trial period in place, and then to dismantle the distillery and move it to another site. The total cost of the demonstration run, the dismantling and re-erection of the distillery, real estate, civil works, etc. is estimated to be $12 million. We project building several such distilleries at a cost of about $20 million each, for a total of more than $100 million, so this is a rather substantial project. If we get into MSW separation, it becomes still larger.

The St. Lawrence distillery has a capacity of 20 million liters of ethanol per year, and would convert waste paper at the rate of 70,000 tonnes per year. We are also meeting with the Paperboard Packaging Environmental Council, and hope they will want a dedicated distillery with paperboard packaging (Rice Krispies boxes, etc.) as feedstock. At this point we have no deep concerns about the supply of feedstock, or the markets for the fuel ethanol. In Ontario, the government has a 13 cents per liter subsidy for ethanol in motor fuel, which is enough to be attractive to distributors and blenders. At the 10% ethanol level, which the regulations permit, ethanol-gasoline blends are a premium grade, and command the same price as premium fuel. This practice is very widespread south of the border. The only problem we anticipate is being able to assure customers of an adequate supply of ethanol in the early stages, so it is a race to get enough ethanol into production: a chicken and egg situation, but one that has been solved elsewhere.

The wholesale value of the product of the first distillery, 20 million liters at 30 cents per liter, has an income of only $6 million. To be adequately profitable, a tipping fee of $60 per tonne would have to be charged. This is much lower than current tipping fees. At the same time as we reduce the volume of MSW to landfill by half, we convert the garbage disposal burden to a handsome profit.

When we have 5 such distilleries based on waste papers, the accumulated surplus profits should generate enough funds to build a garbage separation plant. Such separation plants are expensive. We would take the light fraction and produce ethanol from it, at a good profit. Other products of garbage separation would have to be composted (the soft fraction) or sold as metals, aluminum, etc. Garbage separation plants are operated by municipalities in many countries, Italy, Sweden, Germany, the U.S., etc., and their experience in marketing these other products would have to guide us. In my laboratory at the University of Toronto, we have processed Refuse Derived Fuel from several commercial installations for enriching the paper fraction (the "light" fraction) of MSW to ethanol.

We have an advantage over other researchers in our process for making enzymes. Our enzyme costs will be insignificant. We make the enzyme and simply add the waste paper to the crude enzyme solution. Our best raw material for enzyme production supplies all the nutrients required for enzyme production and fermentation.

CURRENT RESEARCH

Our research is funded, in part, by the Ontario Ministry of the Environment. In our research we have now established a standard procedure for the bioconversion of waste paper to ethanol. It begins with the production of cellulase enzymes followed by addition of waste paper to the mature, crude enzyme solution. After a brief period of saccharification, yeast is added. Ethanol yields are obtained in the range of 350 - 400 liters per tonne of waste paper. While this is a good result,it is only 70 - 80% of the theoretical yield of 500 liters per tonne. Research continues directed to closing the gap, especially by fermenting xylose, which amounts to 14% of the paper, and which is not fermentable by ordinary yeast.

We have now demonstrated two useful, efficient processes for making the main cellulase enzyme which saccharifies paper. The enzyme is made by a fungus Trichoderma reesei in response to an inducer. We have demonstrated the effectiveness of cheap inducers derived from waste newspaper and from starch. The enzymes so made can saccharify 15 kg waste paper for each 1 kg of inducer. Recently we have found that the addition of wheat bran enhances cellulase formation. When wheat bran is substituted for one-third of the starch, 25% more cellulase enzyme is produced.

If the cellulase we make were purchased from commercial manufacturers, it would represent a major cost factor in ethanol production. With our process the cost of cellulase enzyme will be insignificant. Cellulase is the largest component of the cellulase complex, and commercial enzymes as well as our enzymes have an insufficient amount of a second, necessary, enzyme, cellobiase (beta-glucosidase). We are directing attention to the production of cellobiase to reduce this cost.

Much of our recent research has used white office paper as a model substrate to enable us to develop our methods. We are now planning to apply the knowledge so gained to the bioconversion of papers separated mechanically from MSW (the "light fraction", or Refuse-Derived Fuel RDF), to identify and optimize procedures for the use of such a crude feedstock.

FUTURE RESEARCH

This research project needs to be continued to accomplish (i) fine tuning and optimization of the bioconversion process to close the gap between present yields of 350 - 400 liters ethanol per tonne of waste paper and theoretical yields of 500 liters per tonne; (ii) elimination of the need for the second enzyme cellobiase by one of the following: the use of cellobiose-fermenting yeasts; modification of the present cellulase production process, whereby we have already had some modest success; or the production of cellobiase using a different fungus; (iii) application of our process to raw, crude waste paper mechanically separated from MSW as the light fraction or RDF; and (iv) finding the best way to process paperboard packaging, which is a large component of MSW-paper, with relatively unprocessed fibres. These problems are within the range of this laboratory's experience and capability, limited only by the small number of people available to do the work. What we expect to accomplish in future studies is to solve the four problems listed above, and to lay the basis for an Ontario industry for bioconversion of MSW-paper to fuel ethanol, thereby effecting a significant reduction in the volume of MSW going to landfill.

OVERVIEW OF OTHERS' RESEARCH

There are several research groups and pilot plants studying the bioconversion of waste paper or the paper content of MSW to ethanol, in Europe, the U.S., Canada and in Japan. While the best enzymatic saccharification and fermentation pilot plant is that of Institut Francais du Petrole, in Soustons, southern France, they have not yet turned their attention to waste paper, but instead concentrate on hardwoods and agricultural residues. However, in a number of respects their experience would be useful in processing waste paper. In Canada, the best pilot plant employing enzymatic saccharification is that of

Iogen, in Ottawa, which has contributed to research on synthesis of cellulase enzymes and is now studying synthesis of cellobiase, but has not yet begun to study waste paper, as far as we are aware. In the U.S., the Solar Energy Research Institute (SERI) in Golden Colorado, has also studied enzymatic saccharification, but has not, as far as we know, proceeded to pilot plant enzymatic studies, nor to the study of waste paper.

There are also several groups studying the major alternative process, acid hydrolysis of biomass. In the U.S. the Tennessee Valley Authority (TVA), in Muscle Shoals, Alabama, has a pilot plant which is now studying municipal solid waste by acid hydrolysis. In Canada, Professor Chornet, of the Universite de Sherbrooke, Quebec, and St. Lawrence Reactors of Toronto, have the largest such pilot plants. TVA, in anticipation of severe corrosion problems with the sulphuric acid they use for hydrolysis of biomass, has built their equipment of zirconium, a very expensive, and perhaps unnecessary, decision. St. Lawrence Reactors has taken a different approach. They employ hydrochloric acid as the hydrolysis catalyst, and the tubes in their continuous plug flow reactors are made of a Swedish steel which, after more than 5 years of operation, shows no signs of corrosion. The results so far published on the acid hydrolysis process show yields far below those obtained with the enzyme process.

In Europe, a consortium of German and Italian companies has built an interesting pilot plant which follows a partial acid hydrolysis with enzymatic saccharification. This is a very new plant, for which no data are as yet available. In Japan a consortium of companies has built a very elaborate pilot plant which includes every process step that anyone could think of, in the south of Honshu near Miyazaki. The data from it are not impressive. There are many research groups studying bioconversion of biomass to ethanol in Japan, funded by the New Energy and Industrial Technology Development Organization (NEDO), by brewers and distillers, by the Research Association for Petroleum Alternatives Development (RAPAD), and the Fuel Alcohol Research Association (FARA). Also they have very large enzyme production factories, one of which supplied most of the enzyme we used in our early work. The resources available to Japanese scientists involved in biomass research are fabulous. I have been privileged to visit a few of their installations, and am sometimes depressed at the contrast between their facilities and staffing, and ours here. Yet Canada can be proud of the contributions of our scientists to this important area of science and technology, not just in relative terms, but absolutely. In many respects, we are well ahead.

BEHAVIORAL ECOLOGY OF THE EASTERN SUBTERRANEAN TERMITE IN ONTARIO AS A BASIS FOR CONTROL

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ABSTRACT

Subterranean termites are serious structural pests which cause economic losses on the same order of magnitude as fire. Their range in Ontario has steadily increased over the last sixty years despite municipal efforts and a Ministry of Environment-funded grant program to control and contain them. Conventional chemical control is environmentally unacceptable and fails to kill the colony which simply expands its foraging range following chemical treatment. The objectives of our research have been to develop a control strategy to kill whole termite colonies based on sound fundamental knowledge of behaviour and ecology, to demonstrate the ability to extirpate localized populations, and thus to provide a means for municipal-wide termite eradication in Ontario. Through mark-release-recapture studies we have gained a much clearer understanding of the population size, biomass, density, dispersion, territory size and foraging dynamics of northern populations of this species. Populations number in the millions, covering thousands of square meters, with typical densities of about 2,000 per square meter. The caste system, population structure, and seasonal development have been studied. To understand over-wintering, experiments have been conducted on metabolic heat output and termite movement in relation to soil temperature. To understand summer moisture stress, studies were conducted on water imbibition, water transport, and regurgitation on soil and wood for microhabitat humidity control. The effect of soil structure on water availability, rates of tunnelling, and shelter tube construction were investigated. Above-ground foraging on trees is a strong behavioral tendency of *R. flavipes* which is not exhibited by other *Reticulitermes* species in North America. Tree foraging by *R. flavipes* has been further investigated. These biological findings have enabled us to improve aggregation trap designs and trap efficiencies--as many as 42,000 termites have been taken from a single trap and over a half million termites taken from a single plot. A Trap-Treat-Release approach has been investigated in which the trapped termites are treated in ways which induce delayed mortality and transmit slow-acting toxicants or vector microbial biocontrol agents back into the colony. Several borate compounds have been studied as slow-acting transmissible stomach poisons. Some show considerable promise and can be applied either in baits or as cuticular dusts. We have shown that cuticular loading of dusts can be greatly increased with various nontoxic spray paints used as sticking agents. Using sprays to increase loads of borate dust we have found effective lethal ratios of treated to untreated as low as 1:20. Several fungi, viruses, and nematodes have promise as biocontrol agents by the Trap-Treat-Release approach. Physical treatments could be used in conjunction with pathogens. Physical treatments such as gamma and X-ray, and UV irradiation all induce delayed mortality. Inter-colony agonism has not been discovered in Ontario suggesting a possible founder effect and reduced genetic variability which raises the possibility of using treated termites from one colony to invade and vector pathogens or slow-acting toxicants into another colony. Further study will improve trapping and treatment protocols and should make the Trap-Treat-Release approach a viable tool for eradicating termite populations from Canadian cities.

Introduction

The eastern subterranean termite, *Reticulitermes flavipes*, is now known to infest 32 municipalities in southern Ontario. The human population of Ontario is 9,426,100 of which 3,783,161 (40%) reside in the 32 infested municipalities. This termite species was first recorded from Point Pelee in 1929 and its introduction to Toronto is believed to have occurred between 1935 and 1938 (Kirby, 1967). As of 1988, the Toronto Housing Department reported that 5,730 houses had been treated, or about 5% of the total housing stock of the city. These infestations occur on 437 blocks or about 15% of the total city blocks. The average cost for chemical treatment and wood-soil separation in 1988 was $3,272. From 1975 to 1989 the Ontario Ministry of the Environment expended $5.6 million on its Termite Control Program which assisted home owners in covering the cost of treatment. Unfortunately, the spread of termites has not been curtailed and the assistance program has now been suspended. With financial backing from municipal, provincial and federal sources the Urban Entomology Program in the Faculty of Forestry at the University of Toronto was established in 1987 explicitly to conduct applied research for the development of an integrated pest management approach to control the eastern subterranean termite. Dr. J. Kenneth Grace directed the program from 1987 to 1990. Dr. Tim Myles has directed the program since 1990.

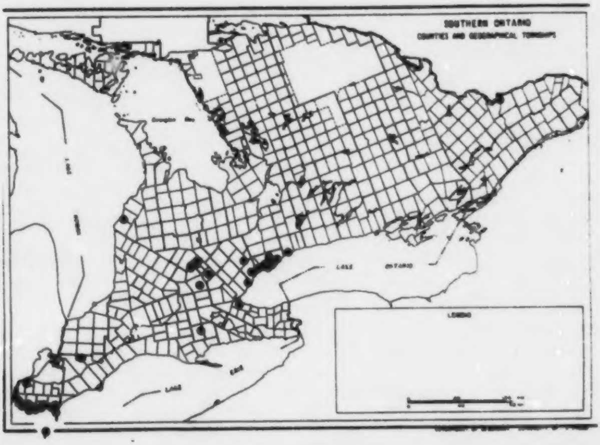

Figure 1. Known distribution of termites in Ontario. Infested municipalities include: Windsor, Malden Centre, Colchester, Kingsville, Leamington, Oxley, Harrow, Mersea, Gosfield South, Amherstberg, Point Pelee, Pelee Island, Dresden, Kincardine, Guelph, Elora, Fergus, Nichol, Woolwich, Kitchener, Hamilton, Oakville, Brampton, Mississauga, Toronto, North York, York, Etobicoke, Scarborough, East York, Pickering, Markham, Old Windham(?).

Population Dynamics and Foraging Behaviour

Esenther (1970) was the first to use the mark-release-recapture method to estimate *R. flavipes* population size in the field. His population estimates varied from 0.32 to 9.5 million termites. Grace et al (1989) and Grace (1990) used similar methods and arrived at estimates of 0.72 to 3.2 million termites. An intensive mark-release-recapture study on a single plot in Kincardine was conducted during the summer of 1990. The daily rate of mortality was adjusted to minimize variation among sequential 4-day estimates. A final population estimate of 4.2 million termites was calculated. The mark-release recapture method is also useful for measuring the foraging territories of colonies. Grace et al reported territories up to 1,091 m^2. The Kincardine study in 1990 indicated a foraging territory of 1,344 m^2. Typical lot sizes on the east side of Toronto are 25 X 100′ indicating that a single colony could overlap five or more entire properties.

Penultimate nymphs overwinter and transform to final stage nymphs and then to winged alates from March through May. Winged alates do develop in Ontario populations but flight records are uncommon due to the inconspicuous nature of most flights. The most abundant reproductive caste in field populations are the nymphoid supplementary neotenics and field evidence indicates a seasonal peak of neotenic development also occurs in the spring. Eggs, small larvae and presoldiers are found through the summer months.

Local populations are undoubtedly more stressed by winter coldness than by summer dryness but in both cases are able to cope well enough in urban-suburban environments. Our experiments have shown that termites do not generate appreciable metabolic heat in aggregations and overwintering therefore depends on finding subterranean hot spots associated with buried wood. Dead trees, stumps, sewer systems and heated structures are likely to provide overwintering hot spots. In the laboratory we typically operate growth chambers at temperatures from 85-90°F at which termites do well and have the highest rates of food consumption. However, the soil temperature preference experiments we have found that when given a choice termites will actually seek much cooler soil temperatures (50-70°F).

Experiments on termite movement relative to soil structure have indicated significant effects of particle size on rates of soil penetration, soil tunnelling, and shelter tube construction. Termites are unable to lift particles heavier than 7 mg (about twice the weight of a large worker) and rarely move particles weighing more than 4 mg. Generally termites are unable to move particles with diameters greater than 1.4 mm and rarely move particles greater than 1 mm in diameter. When soil particles exceed 2.8 mm in diameter the interstices between the particles are just large enough for small worker termites to crawl through. Thus, a mixture of sand composed of particles with diameters ranging from 1.4 to 2.8 mm is completely impenetrable by *R. flavipes*. Below 1.4 mm the rate of tunnelling increases continuously with decrease in particle size. For example, in one experiment over ten days groups of 25 workers tunnelled 0.5 cm through particles 1.4 to 1.18 mm, 4.5 cm through particles 1.18 to 1.0 mm, 7.0 cm through particles 1.0 to 0.85 mm, and 8.5 cm through particles of 0.85 to 0.71 mm. With finer particle sizes the termites penetrated 10 cm in 6 days with particle sizes from 0.71 to 0.5, in 4 days with particle sizes 0.5 to 0.25, and in less than one day with particle sizes below 0.25 mm. Termites were unable to use particles from 1.4 to 1.0 mm for shelter tube construction. Shelter tubes were built slowly and were poorly made when termites were provided with particles ranging in size from 1.0 to 0.71 mm. Shelter tubes were constructed most rapidly (1 cm/day/500 termites) with particles from 0.71 to 0.075 mm. Shelter tubes were most uniform in shape when constructed of particles from 0.25 to 0.075 mm. These experiments suggest that termites probably prefer fine sandy soil (.35 to .075 mm). However, the important effects of soil structure on oxygen availability and soil microorganisms are not known.

Soil particle size also has important effects on water retention and free water availability. Imbibition of hydrostatic water from the soil and water transport have been studied. Termites are able to regulate the microhabitat by transporting water in the crop and regurgitating it for moistening soil and wood. Substantial volumes of water may be involved. Volumes of approximately 10 nanolitres per worker have been measured. Ten water transport trips per worker per day would result in the movement of 100 ml per million workers. Water transport may account for much of the traffic in termite colonies and possibly is critically important in mixing the population. Population mixing has important implications on the use of transmissible toxicants or pathogens for termite control.

Tree foraging by northern populations of *R. flavipes* was first noted by Hagen (1885) in the Boston, Massachusetts area. The importance of this behaviour in Ontario was re-emphasized by Grace and Cooper (1987). In a study of 17,800 trees in Toronto, Cooper (1981) reported the following rates of termite attack: horse chestnut (19%), silver maple (18%), sugar maple (14%), red oak, Poplar spp., and red maple (5%), Manitoba maple, Norway maple (4%), and locust, white ash, elm, tree of heaven and basswood (2% or less). Over the last year we have noted that tree inspection for the presence of external mud shelter tubes is a rapid and effective method of determining the presence of termites on a property. This method was also used to rapidly identify the location of termites on one infested block in Winnipeg in August 1991. Recently numerous observations of shelter tubes on red pine trees have also been made. Shelter tubes are more likely to occur on older trees and trees with rough bark texture. Studies of orientation responses of the termites to wood extractives of various species also indicate the presence of chemical attractants in horse chestnut and repellents in tree of heaven (Grace, 1991).

Aggregation and Mass Trapping of Termites

As individuals, termites are small delicate insects that are easily killed. As a superorganism of millions of sterile workers, thousands of soldiers, and dozens of reproductives occupying a diffuse network of subterranean galleries over a few thousand square meters they are most difficult to kill. The genus in question, *Reticulitermes*, is particularly difficult because of its ecological adaptation as a *xylophagous forager*. Many other kinds of subterranean termites that harvest renewable cellulose resources (such as grass, humus, dung or fungus combs) from a fixed territory are able to establish a permanent nest or mound. It is relatively easy to control termites that build mounds and conspicuous nests. Xylophagous foragers, however, rely on non-renewable, isolated pieces of surface dead wood. The size and dispersion of this food resource, especially in temperate northern parts of the world, is such that their best strategy is never to invest effort in nest-building, but instead, to always be foraging and searching for new resources so that they can move as resource items are consumed. It is also to their advantage to have numerous, scattered, interconnected feeding sites so that they move from place to place adjusting to the ever changing conditions of temperature, soil moisture, and predation from ants. These ecological adaptations have made the control of subterranean termite colonies a challenge that has defied the creative efforts of researchers for decades. It now seems that the key to controlling such colonies is to develop a *delivery system*. With an effective delivery system a variety of toxic or physiologically active materials might be used to kill the colony.

Mass-trapping and direct treatment of the trapped termites appears to be an effective means of delivering toxicant. A relatively recent innovation in applied termite studies has been the development of various traps which employ corrugated cardboard as a food source and matrix for aggregating and harvesting large numbers of termites (La Fage et al, 1983; French and Robinson, 1985; Grace, 1989; Myles and Smith, unpublished). Using traps containing two small cardboard rolls (15 X 4 cm) Grace (1989) reported average collections of 2,612 termites per 3-10 day interval, with maximum catch of 7,622 and total catch of over 200,000 within one 15 day period. Using larger cardboard rolls (15 X 30 cm) placed in PVC shafts 0.5 to 1.5 m deep, we have been collecting an average of 9,200 termites per trap, frequently with 15,000 to 20,000 per trap and with a maximum of 42,542 from one trap! Through the use of cardboard roll traps we were able to trap 526,000 termites in a three week period from our field site in Kincardine, Ontario. In short, it is now possible to trap hundreds of thousands of termites from single colonies within a few weeks.

We have now devised and installed various "trapping system" consisting of rolls of corrugated cardboard of various sizes, in various arrangements, interconnected with buried fibre tubing. The performance of traps is quite variable from site to site, depending on a great number of uncontrollable variables in the urban environment. Refinement of trap system designs will be an ongoing area of research.

Trap-Treat-Release Approach to Colony Annihilation

The centrepiece of our research is to develop a Trap-Treat-Release (TTR) technique for killing whole colonies of subterranean termites. This concept evolved out of previous research on the Bait Block method and mark-release-recapture studies. The technique involves trapping several hundred thousand termites from buried rolls of cardboard. The trapped termites are treated in the laboratory with small doses of chemicals, insect growth regulators, nematodes, or by physical means. A massive number of treated termites are then released back into the colony. A sudden, massive, widespread mortality sets in throughout the extensive soil tunnel network about one to two weeks after release. The growth of saprophytic and pathogenic microorganisms on the dead will disrupt colony homeostasis. Trap-treat-release cycles could be repeated, if necessary, until the whole colony dies.

By the Trap-Treat-Release approach, trapped termites can be treated under controlled conditions. This creates the opportunity for methods of treatment and types of treatment which have never before been contemplated for termites. For example, cuticular dusting or direct topical application of materials is possible. The Trap-Treat-Release technique is a method of quickly treating a large proportion of the colony within a much shorter period of time than is possible by gradual free-choice feeding at baits. Trapping and treating, though somewhat labour intensive, is a far superior *delivery system*. It is necessary that the lethal effect have a delayed onset so that the treated termites disperse back into the colony. With an effective delivery system, a wide array of *delayed-action* lethal treatments might be used, for example: slow-acting toxicants, insect pathogens, parasitic nematodes, insect growth regulators, or physical treatments such as radiation. Various treatments could also be used in combination. In time, the trap-treat-release technique should be perfected as a routine pest control procedure. Alternatively, trapping, on its own, might become sufficiently perfected that it could become possible to exhaustively trap whole termite colonies out of the ground.

Delayed-Mortality Inducing Treatments

Borate compounds are the primary materials that we have investigated so far (Grace, 1990; Grace & Abdallay, 1991, Grace 1991a,b). Several tested compounds applied as cuticular dusts are effective including: disodium octaborate tetrahydrate (Tim-Bor®), barium metaborate (Busan 11-M1), zinc borate, and boric acid. Sodium borate (borax) was not effective. In experiments in which termites were on filter paper in petri dishes, Effective Lethal Ratios (ELRs) of dusted to undusted termites were at least 1:16. Realizing that in the field the ELR will be affected by the loss of dust from the treated individuals as they disperse through the soil tunnels, we decided to evaluate the ELR after various periods of dust loss. To assess the dust loss we have conducted an experiment in which the dusted termites are placed on moist sand for various time periods prior to transferring them to a group of untreated termites. Even after 24 hours of isolation on moist sand the termites carried enough Tim Bor dust to kill untreated termites at a ratio 1:5. This suggests that Tim Bor dust would be an effective toxicant for a Trap-Treat-Release approach if we can trap 20% of the population. As the mark-release-recapture study suggests we can trap around 10% of the colony. Next we studied the serial transmission of Tim Bor. This was done by exposing an initial group of untreated termites to an equal sized group of dusted termites. After one day the exposed termites were transferred to a new group of untreated termites. This was done for a series of 5 days. The experiment showed that after the first transmission by grooming (termites avidly lick each other) there follows one more effective lethal serial transmission, presumably via trophallaxis of gut content. Thereafter no further lethal transmission in the series occurred.

In recent experiments using Tim Bor, we have tried to improve the adhesion of the dust to the cuticle using a nontoxic adhesive marker pen solutions (Sanford, Sharpie® permanent markers). The marker solution has excellent adhesive properties however we were unable to effectively mark and dust large numbers of individuals. We next experimented with spray paints. Depending on rate of application, several spray paints were found that were non-toxic and effectively aided the adhesion of dust. Two or three cycles of spraying and dusting result in maximal loading. We selected a fluorescent orange because this also conveniently marked the treated individuals. Using this method we have achieved effective lethal ratios of 1:20 in petri dishes and 1:10 in soil tunnel arenas which simulate field conditions. Although dusting-spraying is effective and thousands can be treated within minutes, we are now trying to improve treatment by formulating the toxicant directly in an adhesive aerosol spray.

An alternative to the use of insecticides is the use of microbial agents. Zoberi and Grace (1990a) isolated 40 fungal species from *R. flavipes* field material. These included several facultative pathogens and a virulent strain of *Beauveria bassiana* (Zoberi and Grace, 1990b). Recently, we have also initiated studies with Dr. Martin Hubbes of the Faculty of Forestry at the University of Toronto on various nematodes that are pathogenic to subterranean termites. In collaboration with Dr. David Levin of the Department of Biology, York University we are undertaking preliminary investigations of several entomogenous viruses. Several non-occluded forms of nuclear polyhedrosis viruses and one entomopox virus have been found that infect and kill *R. flavipes*.

Direct exposure of termites to physical treatments is possible in the Trap-Treat-Release approach. Physical treatments are of considerable interest because they do not produce immediate behavioral impairment and do not burden the insect with carrying a chemical load (allowing the termites to disperse widely from the release point). Physical treatments might be used alone or in conjunction with transmissible chemical or microbial agents. We have investigated various physical treatments as methods of inducing delayed mortality. Short wave UV (9 watts) induced 100% mortality in 9 days after 2-3 minute exposure. With gamma radiation from a Co^{60} source LD_{50} from 3 to 28 days were obtained with exposures to 3064 to 383 Rads. Portable gamma emitters with Co^{60} and Ir^{192} pellets required 1 and 2 hours of exposure time respectively to induce 100% mortality in 12 days. Termites were X-rayed with a portable 200 KV unit which required only 25 minutes exposure to induce 100% mortality in 10 days. UV is least hazardous form of physical treatment and requires the shortest exposure time. However since gamma and X-rays could penetrate cardboard and soil they could be used in an "aggregate and irradiate" strategy. A portable X-ray or gamma emitter could be mounted on a small wagon and driven to any location. It could then be used to irradiate the aggregated termite *in situ* in the aggregation traps without even removing the trap from the ground. Two or three exposure cycles might be enough to kill a colony. This would entail relatively small labour costs, and would leave no toxic chemicals in the soil.

Benefits of Research

Present methods of control are property-specific and heavily dependent on large gallonages4 of persistent pesticides applied as a chemical barrier in the soil around an infested structure. This method is usually effective for protecting a given structure (although re-treatment is often required). However, the chemical barrier method is almost never effective in killing the termite colony which simply moves from the treated site to an adjacent untreated property. By the Trap-Treat-Release technique it will be possible to eradicate isolated pockets of termite infestation in Ontario municipalities rather than simply protecting properties one at a time. Eventually it may be possible to eradicate termites block by block to re-establish "termite free zones" in Metro Toronto.

With further development, the Trap-Treat-Release technique will become an integral component in urban pest management. Effective development of the Trap-Treat-Release method will substantially reduce or eliminate the amount of persistent pesticide used for subterranean termite control. By reducing the need for termiticides, it will dramatically lower the load of persistent toxicants in the urban environment. The reduction of termiticide treatments will also decrease the long-term health hazard to residents of termiticide-treated homes, arising from lingering vapours in in-door atmospheres and from accidental contact with treated soil. It will also reduce or eliminate the health hazards to applicators of termiticides arising from spills and misapplications.

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F5

The Development of Reliable Treatment Systems for Milkhouse Washwater; M. Anderson and P.H. Groenvelt, University of Guelph, Guelph, Ontario

Introduction

Research conducted by the Upper Thames River Conservation Authority has identified the improper disposal of milkhouse wash water as one of the most serious sources of agricultural pollution in the province, amounting to over 200 tonnes of phosphorus entering rivers annually in Southern Ontario alone. This is approximately 12% of the estimated load to Lake Erie from agricultural land in Ontario, assuming all this phosphorus reaches surface waters. Compounding this is the fact that 63% of this phosphorus is soluble reactive phosphorus, and thus much more available for algal growth than phosphorus pollution from run-off (Miller et al., 1987). In addition to phosphorus, this effluent usually contains large amounts of residual milk which is a strong source of BOD and bacterial pollution.

A large part of the problem is that farmers who do not have liquid storage facilities currently lack a reliable method of disposal. In the past, the Ontario Ministry of Agriculture and Food has recommended the installation of septic tank-treatment trench systems on such farms. However, a large proportion of these systems which were installed have failed, and as a result have acquired a reputation within the farming community as being quite unreliable.

The primary goal of this research project is to develop simple modifications to the milkhouse septic tank system design or on-farm practices which will render these systems reliable for at least 25 years.

In order to achieve this goal, the direction this research project has taken in the last six months is not so much to modify the treatment trench disposal system, as to modify the characteristics of the effluent so it will be less prone to cause failures of these systems.

Farmer survey:

A mail survey was sent out in late November, 1990, to 128 farms which had installed milkhouse treatment trench systems under the OSCEPAP II program. Of the surveys sent out, 89 responses were received. The aim of this survey was to identify factors which were contributing to the failure of the treatment trench disposal systems and to determine their relative importance. Included in the survey were all the conceivable factors which might affect the lifespan of these systems, including: soil type, water use, milk spills, septic system design, length of milk pipeline, etc. An example the survey is found in appendix I.

Survey Results:

Number of surveys sent out: 128
Number of returns: 89
Number of case studies: 104
(many surveys provided information on more than one system)

Number of systems still functioning: 65

-which are diverting rinse water: 28
-which are not diverting rinse water: 29
-which are not using a pipeline: 8

Number of systems which have failed: 39

-which were diverting rinse water: 19
-which were not diverting rinse water: 18
-which were not using a pipeline: 2

Details of disposal system history:

	For systems still functioning	For failed systems
Ave. lnth. pipeline	210 feet	181 feet
Ave. # of cows	36	36
Ave. est. water use	129 gallons	106 gallons
Ave. drain time	6.8 minutes	5.6 minutes
Using air injectors	54%	54%
Any milk spills?	26%	33%
Ave. vol. settling tks.	722 gallons	475 gallons
With baffled outlets	78%	62%
Ave. length of trench	264 feet	223 feet
Ave. yrs. btwn. pumpings	2.6 years	1.7 years
Ave. date of install.	1987	1980
Requested survey results	74%	96%

Statistical analysis was carried out on those case studies involving a failed system. A multiple regression was set up involving the following factors:

- water use
- Number of settling tanks
- volume of settling tanks
- length of weeping bed
- clay content of soil
- milk spills
- diversion of rinse water
- hydraulic loading rate (water use/length of weeping bed)

The response used in this analysis was the lifetime of the system in years. The only factors which appear to significantly affect the lifespan of these systems is the diversion of rinse water and hydraulic loading rate. Essentially this means that if farmers use less water and exclude the rinse water from the septic systems, these systems will work significantly better.

The Effect of Diverting Rinse Water on Effluent quality:

A central hypothesis of this research is that the diversion of pipeline rinse water will reduce the formation of a thick soil clogging mat in the weeping bed. Research regarding household weeping bed systems has shown that the extent to which a clogging mat develops is accelerated by effluents of higher organic strengths and by higher hydraulic loading rates (Jones and Taylor, 1965; Laak, 1970; Siegrist, 1987). More specifically, the development of this mat seems to be directly related to the cumulative loading of BOD and total suspended solids (Laak, 1970; Otis, 1985; Siegrist, 1987).

In January, 1991, an experiment was conducted on a farm east of Peterbourgh, Ont. in order to determine what effect the diversion of rinse water would have effluent quality and therefore on the organic loading rate to the weeping bed.

Since 1978 this farmer had installed two weeping bed systems and two dry wells in order to treat his wash water, none of which lasted more than one year. He was currently allowing the settling tank to overflow and run down into a gully. He had also never diverted his rinse water.

We determined that since he had recently installed a semi-solid manure system, a solution in his case involved only the re-routing of the drain in his milkhouse sink to drain into his manure gutter . However prior to this, he consented to begin diverting the pipeline rinse water in order to investigate the effect this would have on the quality of the effluent in the settling tank. Weekly samples were taken from the tank for a period two weeks before to two weeks after he began diverting the pipeline rinse water. Samples were analyzed for BOD and TSS with results shown in fig 1 and 2 in the appendix. TSS showed a 85% reduction within one week of diversion and an 89% reduction over two weeks. Similarly, BOD values dropped by 42% within one week and 74% within two weeks.

While this farmer is now putting his milkhouse wash water into liquid manure storage, he plans to continue to divert the pipeline rinse water as he feels it is good feed for his calves.

Water use Studies:

It is well documented in scientific literature relating household weeping bed systems that a reduction in the hydraulic loading rate will reduce the likelihood of system failure, independent of the organic loading rate (Seigrist, 1987; Sharpe et al., 1984). This is presumably due to more efficient biodegradation of organic matter in the weeping bed when water is not continuously ponded in the trenches.

Unfortunately, there is very little literature relating to water use by modern dairy operations. In addition, from the survey results, there is no correlation between estimated water use and pipeline length, pipeline diameter, number of cows or even the number of wash cycles per day.

There are two possible explanations for this lack of correlation: either farmers are very bad at estimating their water use or there is another factor which dominates water use which was not included in the survey.

In addition to improving the function of milkhouse weeping bed systems, reducing water use would have several other benefits which would attractive to farmers. Approximately 2/3 of the water farmers use for pipeline washing is hot water. A reduction in water use would bring a considerable economic savings in terms of hydro use and also in terms of cleaning chemical use. Hydro and chemical costs typically range into the thousands of dollars per year per farm.

In order to investigate the factors which affect water use, several milkhouses have been instrumented with meters to measure hot water use, total water use and hydro use by the milkhouse hot water heater. Farmers involved in these studies have agreed to read these meters every day and have been encouraged to experiment on their own to develop simple ways to reduce water use.

The water meters used were Neptune Bronze 1/2" water meters obtained from Canada Valve in London, Ont. and rated accurate within 1%. The hydro meters were obtained from Waterloo North Hydro for a nominal fee and are also rated accurate within 1%.

Several mechanical modifications will be investigated for their effect on water use. Specifically, "air injectors" for pipeline circulation, and "wash manifolds" to more efficiently use the water in the milkhouse sink, are both commercially available and are claimed to reduce the amount of water used for pipeline cleaning.

Water Use Study Results:

At the time this report was written, three farms were participating in this study with two others as yet to be instrumented. Results for two of the participating farms are seen in figs. 3 and 4 in the appendix.

Substantial water savings have already been achieved on two of the participating farms. Bill Irwin had for many years been using approximately 150 l/cycle which would amount to approximately 1300 litres of water per day. During a farm visit in Nov. 1990, his excessive water use was discussed and he adjusted the level to which the water in his sink filled. This simple adjustment, involving only a length of hose in his milkhouse sink, reduced his water use by over 34%. In the spring of 1991, a similar adjustment was made resulting in a further 47% reduction, for a total water use reduction of 65% or 850 litres of water/day.

From measurements of hydro consumption/l of hot water, this will result in an energy savings of 11,500 KWH/yr. amounting to approximately $800/yr.

Ron Forbes, another farmer who is participating in this study, has cooperated in redesigning a milkhouse sink which has reduced his water use by approximately 40%. This will result in total water savings of 275 litres of water/day and hot water savings of 62,500 litres/ yr. Energy savings will amount to approximately 3,050 KWH/yr. or $210/yr.

In addition to looking at general water use and investigating methods to achieve reduction, we will also be comparing farms for energy efficiency as some farms are using heat exchangers to recover heat from the bulk tank. Results for energy consumption in relation to hot water use are given for two of the participating farms in fig 5 and 6. It is apparent from these figures that heat exchangers offer substantial energy savings. Ron Forbes, who has a heat exchanger is using 47.7 KWH per cubic metre of hot water. Bill Weiker, who is not using a heat exchanger, is consuming 75.0 KWH per cubic metre which is 36% less efficient.

Research in this area will continue in the following year.

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F6

POTENTIAL METHODS OF REVEGETATING THE KAM-KOTIA TAILINGS SITE, TIMMINS.

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The Kam-Kotia mine/mill complex is located 15 km northwest of Timmins. Following closure in 1972, the property reverted to the Crown without rehabilitation. The area requiring revegetation is a sulphide-rich, acid-generating tailings deposit covering 275 hectares, including impounded areas where the tailings form a consistently deep layer and non-impounded areas where the thickness of tailings is highly variable. Acid mine drainage from the tailings has a pH of around 2.5, and is high in arsenic, zinc and copper.

Prior studies (e.g that by the D. Comrie Consulting Ltd (1987)) recommended sophisticated and costly solutions. In 1990, the author was funded by the Kam-Kotia Steering Committee to carry out a number of small-scale trials employing varied "low-tech", low-cost revegetation techniques.

MATERIALS

a. Growth media and base materials

Pit-run gravel was used both as a growth medium and as a base material. "**Loam**" - an approximately 50:50 screened mixture of "red loam" and "black loam" - was used as a growth medium (although **red loam** was also used in some treatments).

Peat moss was either used on its own as a growth medium, or else was mixed into the upper few centimetres of the gravel, where its function was to improve moisture-retaininfg capacity and to provide both a nutrient source and a nutrient-adsorbing material. **Bog peat** served both as an oxygen-barrier and as a base for living bog-sods collected at the same bog.

b. Neutralizing agents

Ground Dolomitic Limestone contained 2% calcium and 12% magnesium with a $CaCO_3$-equivalent of 101%. It was ground such that 5.4% passed a 100 mesh screen and 100% passed a 10 mesh screen. Unless stated otherwise, the application rate was 4 t/ha (1.6 kg per 4 m^2 plot). **Sewage Incinerator Ash** is a by-product of a Toronto sewage treatment plant, in which the sludge removed during the treatment process is burned. The major constituent of the ash (38%) is a calcium magnesium phosphate ($Ca_7Mg_2P_6O_{24}$). Unless stated otherwise, the application rate was 2 t/ha (0.8 kg per 4 m^2 plot). **Marl** was obtained from the Pup lakes (formerly Twin lakes) area in west-central Thorneloe township, District of Temiskaming. It contained approximately 87% $CaCO_3$ and 2.2% $MgCO_3$. Unless stated otherwise, the application rate was 4 t/ha (1.6 kg per 4 m^2 plot).

c. Fertilizers

A 6-24-24 agricultural-grade fertilizer was used at a rate of 400 kg/ha (160 g/4 m^2plot)

d. Plant material

i. **Seeds** The grass-legume seed mix had the following constitution*:

Agrostis gigantea	Redtop	10%
Festuca arundinacea	Tall Fescue	30%
Phleum pratense	Timothy	20%
Poa compressa	Canada Bluegrass	10%
Poa pratense	Kentucky Bluegrass	20%
Trifolium hybridum	Alsike Clover	10%

* Seed of Birdsfoot Trefoil (*Lotus corniculatus*) was not available at the time, but will be dormant-seeded onto the plots in the late fall of 1991.

The seed mixture was sown at a rate of 30 kg/ha (12 g/ 4 m^2 plot), and lightly raked into the plot surface.

ii. **Transplanting stock**

The following plant material was collected from acid, metal-contaminated soils in the Sudbury area, where there was some evidence of their acid- and metal-tolerance:

Tufted Hairgrass (*Deschampsia caespitosa*)
Redtop (*Agrostis gigantea*)
Wool Sedge (*Scirpus cyperinus*)
Dwarf Birch (*Betula pumila*)

All samples were collected with a large portion of native soil attached to the roots.

METHODS

a. Seeded Plots were set up on the well-drained North Impounded Tailings. Their dimensions were 2 m x 2 m, with a 0.5 m sloped buffer zone. They were set up in triplicate, using a randomized block design. Plots fell into three categories:

i. **Direct amelioration** of tailings. Current knowledge of the chemistry of the tailings strongly suggests that direct revegetation, however effective the neutralizer, will not succeed in the long run. It was felt, however, that this hypothesis should be checked experimentally. Dolomitic limestone and marl were applied at 20 t/ha and ash at 10 t/ha, respectively, and raked into the surface of the tailings.

ii. Use of a **gravel covering or overburden**. The rationale for the use of coarse gravel as a covering for the tailings is based on its porosity. Upward movement of acid ground-water by capillary action is low, and acid ground-waters are easily washed out by rain. Disadvantages of this growth medium are the low nutrient content and nutrient-retaining capacity, and the low moisture-retaining capacity. However, past experience has shown it to be an effective covering, both with (Spires, 1975) and without (Michelutti, 1974) a loam covering. The plots were constructed with gravel alone, gravel topped with commercially available peat moss which was worked into the top 5 cm of the gravel, gravel topped with locally-obtained red loam and gravel topped with the "loam" described above. Depth of both gravel and covering (where employed) were varied. In each case, one of the three neutralizers was raked into the surface, along with the standard fertilizer.

iii. Plots based on a loam covering. In each case, one of the three neutralizers was raked into the surface, along with the standard fertilizer.

b. Transplant plots fell into the following categories:

i. **Direct transplants.** Potentially tolerant Sudbury plants were transplanted, in a block of their own soil, into transects having three treatments - untreated tailings, limed tailings and gravel over tailings.

ii. Plots involving the use of a living bog-sod cover. In these plots, blocks of bog peat, complete with living vegetation, have been placed on top of the tailings. In this case, no neutralization, fertilization or seeding was carried out since the intention was to have the bog plants survive in the peat block, which will itself impede oxygen penetration and tailings oxidation. Native peat from the bog was also used to form the 0.5 m shoulder.

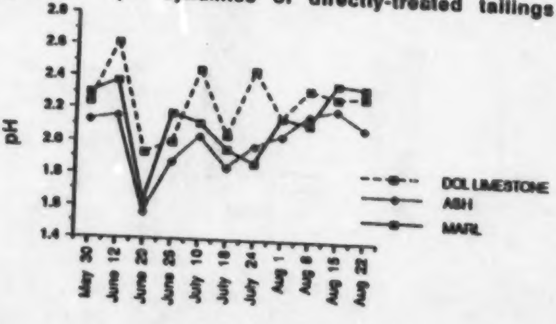
c. Monitoring A photographic record of the plots was obtained several times during the summer of 1991. Soil samples were obtained from the surface 10 cm of each plot on a weekly basis, and analysed for pH and moisture content. Biomass was determined in August by harvesting the vegetation on 50% of each plot, drying it and weighing it. Cover material samples were retained for possible future metal analysis .

RESULTS

a. Seeded Plots

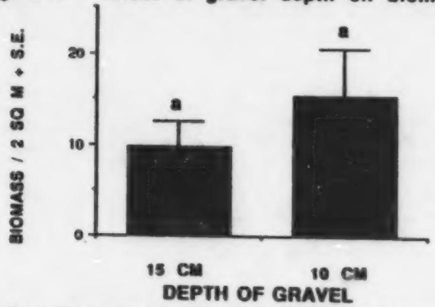
i. **Bare tailings.** As predicted, there was no plant survival on directly-treated plots, although there was some germination and short-term growth. By the time monitoring began in May following treatment the previous fall, the pH was already very low, and, despite fluctuations, it remained so (Figure 1).

Figure 1 - pH dynamics of directly-treated tailings



ii. **Gravel-covered tailings.** On gravel-covered tailings, biomass production was low, but survival was, in most cases, reasonable. As shown in Figure 2, biomass production was somewhat less on 15 cm of gravel than on 10 cm, but not significantly so.

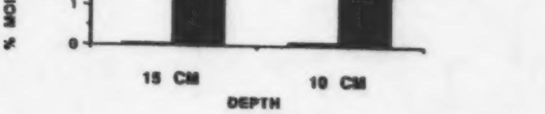
Figure 2 - Effect of gravel depth on biomass production



Bars bearing the same superscript are not significantly different at the 5% probability level.

The reduced growth on the deeper gravel was presumably due to greater exposure, both in terms of drying and of wind-borne tailings abrasion. Figure 3 shows comparative moisture levels at a dry time and a moist time, respectively. Moisture content is consistently higher in the 10 cm gravel plots, but the difference is not significant statistically.

Figure 3 - Surface moisture in relation to gravel depth



Figures 4 & 5 show the changes in pH that occurred in the top 5 cm of the gravel plots. pH dropped sharply at first , but levelled off between pH5 and pH6. There semed to be very little difference in pH dynamics between the 15 cm and 10 cm gravel plots .

Figure 4 - Surface pH dynamics in 15 cm gravel plots

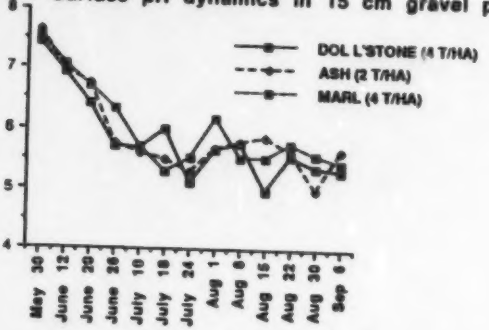
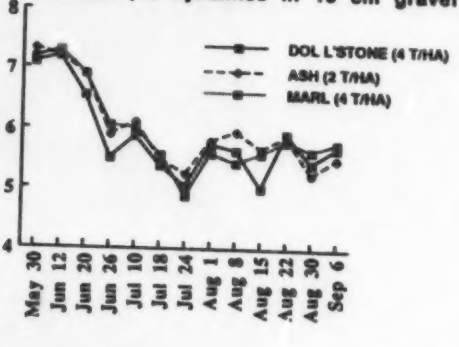
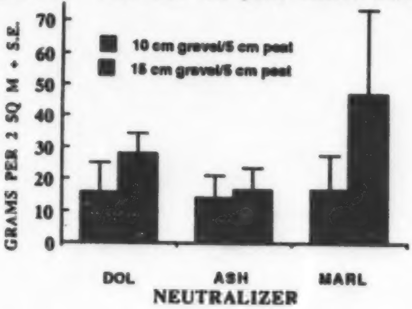


Figure 5 - Surface pH dynamics in 10 cm gravel plots



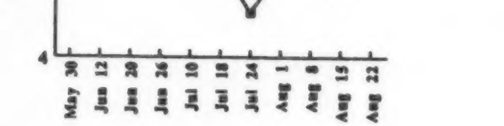
iii. **Gravel-covered tailings with peat worked into surface.** Contrary to the situation described for pure gravel, growth was better on 15 cm of gravel with 5 cm peat worked into the surface than on 10 cm with the same amount of peat (Figure 6).

Figure 6 - Biomass on peat mixed into gravel



It is possible that the greater proximity of the peat's capillary-enhancing properties to the tailings surface led to great upward movement of acid in the shallower gravel, a hypothesis that is supported by the pH trend shown in Figure 7.

Figure 7 - pH dynamics on peat-gravel plots



iv. **Loam.** On loam-covered tailings, a gradual drop in pH occurred, but only in the plot with a 5 cm cover did the pH drop below 6.0 . This is illustrated for the marl treatments in Figure 8.

Figure 8 - pH dynamics on marl-treated loam

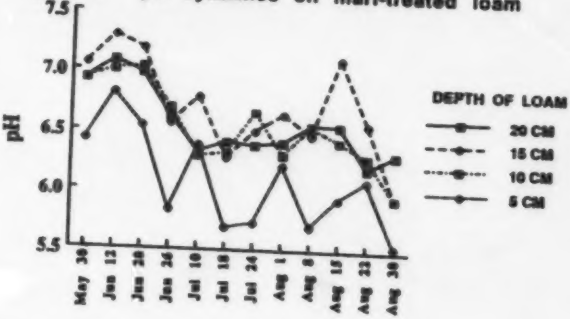
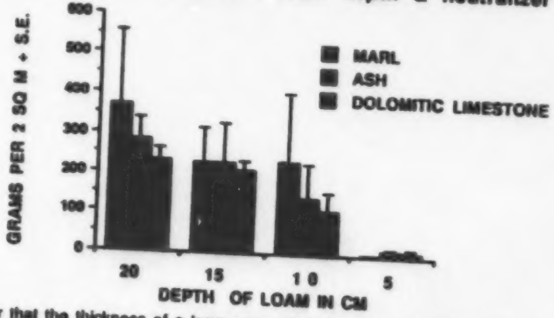


Figure 9 summarizes biomass production on loam.

Figure 9 - Biomass v loam depth & neutralizer

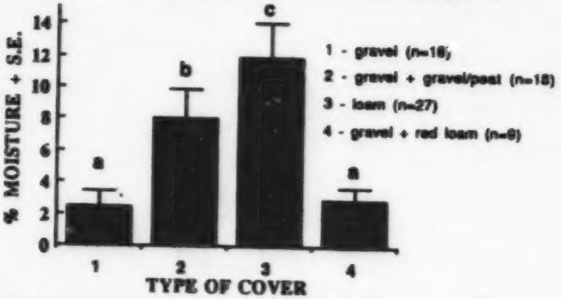


It is clear that the thickness of a loam cover should not be reduced below 10 cm. Effectiveness of neutralizers appears to follow the sequence of marl>ash>dolomitic limestone, but it must be remembered that the marl contains phosphorus, and could be playing a fertilizer role.

v. General

Figure 10 shows mean moisture levels of the different covers for most of the summer period. Not surprisingly, loam has the best moisture-retaining properties.

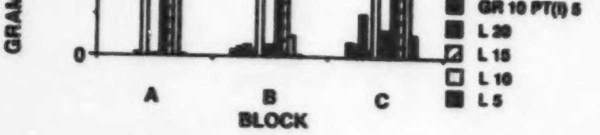
Figure 10 - mean surface moisture, June 26-Sept 13



Bars with the same superscript do not differ significantly at the 5% probability level.

From Figure 11, it is clear that Block C, which is located within the shelter of dead treetops, has a more favourable environment than the other blocks. It is also clear that a 15-20 cm layer of loam is likely to give the best biomass, with 10 cm of gravel covered by 10 cm of loam the second-best.

Figure 11 - Treatment & block effect on biomass



Future observations on the upward-movement of acidified tailings water will probably determine whether the gravel-loam combination is indeed preferable to the loam alone.

b. Transplant Plots

i. Direct transplant plots. No quantitative data are available at this time, but it can be stated that there was a good survival rate overall. Dwarf Birch was most succesful on the North Unimpounded site, and Wool Sedge on the moist South Unimpounded site. Tufted Hairgrass and Redtop did well in all sites. A quantitative assessment will take place in 1992.

ii. Bog Sod Plots. All bog species remained vigorous.

CONCLUSIONS

While one year is too short an experimental period to be able to draw firm conclusions, it appears that it may be feasible to use of a cover material to revegetate the well-drained portion of the Kam-Kotia tailings. Preliminary results suggest that a loam covering or a gravel covering topped with loam would be most effective, but at least one more season of observation will be required to determine the relative vulnerability of different cover combinations to upward movement of acids.

The use of metal-tolerant transplants from the Sudbury area also shows some promise. The bog-sod transplant approach also shows promise, but it is probably neither economically feasible nor conservationally desirable to use this technique on a large scale, unless plans to develop the horticultural peat industry in Northern Ontario come to fruition.

ACKNOWLEDGEMENTS

A number of individuals have assisted in this project, and the author wishes to acknowledge the considerable contribution of those most recently involved, viz. Daniel Archambault, Derek McHale, Allan Petryna and Bryan Tisch.

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SOLID WASTE PRODUCTION AND MEASUREMENT IN LAND BASED CULTURE OF RAINBOW TROUT (*Oncorhynchus mykiss*)

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ABSTRACT

Solid waste is produced in land based trout culture in the form of uneaten and undigested feed. Undigested feed is equivalent to approximately 0.27 grams dry matter faecal waste per gram of dry pelleted fish feed. At this rate of production, distribution between suspended and settled solid wastes is variable with total solids equivalent to concentrations of 100 ppm or less in the flow through fish rearing tanks. Higher concentrations occur when tanks are cleaned, and generalized estimate of solid waste quantities due to uneaten food are not known. At concentrations of 100 ppm and less, individual solid particles settle initially as discrete particles without interference between particles in Type I settling. Subsequent Type II settling occurs as concentrations increase with depth, followed by Type III and Type IV settling when compression of settled solids produces concentrations of 50,000 ppm. Four types of settling were investigated using fresh faeces from 300 gram (0.66 pounds) rainbow trout held at a stocking density of 35 kilograms per cubic meter (2.2 pounds per cubic foot). Type I and Type II settling were observed to determine that 90% of initial concentrations, at 30 ppm and less, settled from suspension in ten minutes or less. For similar initial concentrations Type II settling was observed in Imhoff cones and resulted in flocculated concentrations in excess of 20,000 ppm within 20 minutes. Subsequent Type III and IV settling produced concentrations in excess of 50,000 ppm within one hour. The preceding experiments provide the basis for current investigation of the settling characteristics of solid faecal waste produced by rainbow trout as they grow from an initial size of 25 grams (.9 ounces) to 250 grams (0.6 pounds). Results will be applied to the development of design guidelines for sedimentation tanks required at different stages of fish growth. Both ongoing studies and prerequisite investigations are funded by The Ontario Ministry of Agriculture and Food and The Ontario Ministry of The Environment.

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BACKGROUND AND OBJECTIVE

Undigested feed and uneaten feed appear as solid waste in land based trout culture. The quantity of uneaten feed differs with feeding method but generalized estimates of solid waste due to uneaten feed are not available. Undigested feed is equivalent to 0.26 to 0.28 grams dry matter faecal waste per gram of dry pelleted fish feed (Willoughby et al., 1972; Windell et al., 1978; Butz and Vens - Cappell, 1982; Clark et al., 1985; Farrell, 1990).

Waste solid particles that are heavier than water can be removed by gravity settling in controlled settling zones (Wheaton, 1977; Metcalf and Eddy, 1979; Boersen and Westers, 1986). The primary purpose of controlled settling is to produce a clarified effluent from the controlled settling zone, but the production of a sludge that can be easily removed and disposed of is also necessary.

In the case of municipal sewage, design of settling works is based upon theory about four distinctly different settling processes that occur in the treatment of municipal sewage. Individual particles in dilute suspensions settle as discrete particles, in Type I settling, without joining of individual particles to form coalesced flocs. Flocs have greater mass and higher settling velocities than individual particles and settle more quickly as attributed to Type II settling.

As coalesced flocs settle downwards, concentrations increase and interference between flocs occurs at concentrations between 2800 and 6500 parts per million (Fair et al., 1968). At such concentrations settling velocities decrease and interference between flocs results in mass settlement distinctive of Type III settling. In Type IV settling the concentration of interfering flocs increases, structure is formed and compression of settled solids follows as solids are continuously added to form concentrations in excess of 50,000 parts per million.

Concentration of solid waste in the flow through trout rearing operations is variable over a representative range of 0 to 104 parts per million having an average concentration of 7 parts per million (Liao, 1970). At such low concentrations Type I settling would occur during initial stages of the settling process.

Thomson (1986) and Stechey and Trudell (1990) investigated the settling characteristics of rainbow trout solid waste mixed in suspensions at initial concentrations an order of magnitude greater than the initial concentrations observed by Liao in 1970. The studies by Thomson and Stechey demonstrate the occurrence of Type II and Type III settling of solid waste from rainbow trout. Evidence of Type IV settling is available from studies by Boersen and Westers (1986) who report settled solid waste concentrations in excess of 50,000 parts per million typical of Type IV settling.

The preceding independent studies show that the four settling processes in municipal sewage occur in settling of solid waste from rainbow trout. However, the characteristics of process in each of the four types of settling of rainbow trout solid waste are imperfectly understood at this time. Also current studies do not include application of proven experimental methods to the analysis of overall process in settling of solid waste from rainbow trout.

It is not evident that known experimental methods can be successfully applied to the analysis of process in settling of solid waste from rainbow trout. Nor is it clear that existing settling theory can be applied to the design of settling works in land based trout culture.

The objective of this study is to describe a preliminary investigation of Type I, II, III and IV settling of solid waste from rainbow trout using current experimental methods. Experimental results will be interpreted for application of existing settling theory to design of settling works in land based trout culture.

METHOD

Fresh settled faecal solids were collected from rainbow trout (Oncorhynchus mykiss) of average size 300 grams (0.66 pounds) held at a stocking density of 35 kilograms per cubic metre (2.2 pounds per cubic foot). At this density break-down of faecal pellets due to fish movement was not evident. Solids settled to the bottom of the holding tanks and were captured in sampling hoppers at the bottom of the tanks.

Tests for Type I and Type II settling were completed in a settling column 1000 mm (39.3 inches) deep and 150 mm (6 inches) inside diameter. Dilute suspensions at uniform initial concentrations of 15 to 30 parts per million of fresh faeces were sampled at one minute intervals from a sampling port at a depth of 750 mm (30 inches). Conventional methods (Camp, 1946) for the analysis of Type I and Type II settling in municipal sewage were applied to calculate settling velocity of solid particles, at a depth of 750 mm, in relation to the concentration of particles remaining in suspension at a depth of 750 mm (30 inches).

As background to analysis of Type III and Type IV settling, dilute suspensions at uniform initial concentrations of 15, 20, 25, 30 parts per million were settled in one litre Imhoff cones. These tests provided estimates of the volume occupied by the uncompressed settled solids, and their concentration at the transition between Type II and Type III settling.

Guided by results from the Imhoff cone tests, concentrated suspensions at uniform concentrations of 19,600, 20,200, 21,800 and 24,100 parts per million were observed to settle in a 300 mm (12 inch) graduated cylinder. Rate of settling was determined according to observed downwards movement of the interface between "clear" liquid and concentrated solids below the interface. Observations were analyzed according to the method developed by Talmadge and Fitch (1955) for differentiating Type III and Type IV settling of solids in municipal sewage.

RESULTS

In the tests for Type I and Type II settling, standard settling column analysis of dilute suspensions was limited to observations at a single depth of 750 mm. (30 inches). Results were analyzed as proposed by Camp (1946) for municipal sewage, and showed that the concentration of suspended solids decreased systematically with time. Settling was rapid with removal of over ninety percent of suspended particles within ten minutes. The corresponding average particle settling velocity was 0.1 metres per minute.

Consistent with results from the Imhoff cone samples, tests for Type III and Type IV settling were based upon suspended solids concentrations in the range 19,800 to 24,100 parts per million initial concentration. Results were analyzed as proposed by Talmadge and Fitch (1955) for municipal sewage. For the test range in initial concentration, the initial settling velocity remained constant for approximately three minutes. The observed range in initial settling velocity was 4.3 to 2.1 metres per hour and initial settling velocity decreased with increasing initial concentrations.

After approximately three minutes the settling velocity decreased systematically in all cases. By fifteen minutes the transient settling velocity was reduced to near-zero constant rates that occur during compression of settled flocs.

DISCUSSION AND CONCLUSIONS

In this study, current methods for the analysis of settling in municipal sewage were used to investigate settling in dilute and concentrated suspensions of solid waste from rainbow trout. Settling of dilute suspensions was examined by conventional settling column analysis which is based upon theory about Type I and Type II settling (Camp, 1946). Analysis produced estimates of percentage removal of settled solids in relation to depth and time, and estimates of particle settling velocity. These settling characteristics determine the design of effective settling tanks for removal of solids from effluent of land based trout culture operations.

Settling of concentrated suspensions was analysed according to methods proposed by Talmadge and Fitch (1955) for municipal sewage. This analysis is based upon theory about Type III and Type IV settling and establishes relationships between settling time and resulting concentration of thickened settled solids deposits. Thickening characteristics of settled solids deposits determine the size of settling tank required to produce optimum concentrations in compressed solids for effective removal.

Results from the study are preliminary as they refer to a specific fish size, stocking density and diet. Within these constraints, current theory about settling in municipal sewage can be applied to determine the settling characteristics of dilute and concentrated suspensions of solid waste from rainbow trout. These settling characteristics determine the basis for design of effective settling works.

According to the results of the preliminary study current experimental methods will be applied to determine the settling characteristics of solid faecal waste produced by rainbow trout as they grow from an initial size of 25 grams (0.9 ounces) to 250 grams (0.6 pounds). Results will be applied to development of design guidelines for solids settling and solids thickening works required at different fish size in land based cultures of rainbow trout.

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P8

Field and Laboratory Evidence of *In Situ* Biotransformation of Tetrachloroethene to Ethene and Ethane at a Chemical Transfer Facility in North Toronto[1].

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INTRODUCTION

A potential real estate transaction initiated a groundwater investigation at a 4.5- acre chemical transfer facility located in North Toronto. The fenced facility is comprised of small office, boiler and weigh scale building, road with turnabout, railway spur line, and above- and below-ground transfer lines (Figure 1). Organic solvents are delivered to the site by rail and transferred by below- and above-ground pipes to the above-ground tank farm and eventually to tanker trucks. Both the previous and current owners of the facility stored and transferred similar organic solvents (methanol, methyl ethyl ketone, vinyl and ethyl acetate, butyl acrylate) with one notable exception. The previous owner had stored tetrachloroethene (PCE) at the site approximately 10 years ago. Preliminary groundwater investigations revealed both free and dissolved PCE, and the dechlorination intermediates of PCE had contaminated the groundwater below the facility. The absence of PCE, or its intermediates, between the former PCE storage tank and the spur line suggests that small amounts of free-phase PCE were released during the coupling and uncoupling of railway tanker cars, and not from the above-ground storage tank.

Pumping test data indicated that pumping could effectively contain the dissolved PCE on site, but the hydraulic conductivities of the aquifer were too low for the feasible application of pump and treat strategies to reduce source area PCE concentrations. However, the presence of dechlorination products suggested that anaerobic biotransformation of PCE might be an attenuating mechanism, one that could be exploited in remediating the site if vinyl chloride (VC) was not accumulating. As a result we undertook a field and laboratory investigation to determine if VC was being mineralized or biotransformed to innocuous end products. If VC was being biotransformed, we wished to understand the physical, geochemical, and microbial processes that promote the conversion of PCE past VC. This paper presents our initial field and laboratory data that provide evidence of *in situ* biotransformation of PCE to ethene.

MATERIALS AND METHODS

Details of groundwater and sediment collection, geochemical and geological analysis, microbial analysis and microcosm studies are presented elsewhere (Major *et al.*, 1991[2]).

Geochemistry Parameters included in the analysis included cation/anion scans, dissolved organic carbon (DOC), metals, alkalinity, Ph, eH, dissolved oxygen (D.O.), temperature, hydrogen gas, hydrogen sulfide, C1-C3 gases (methane, ethane, propane), volatile fatty acids (notably acetate), chlorinated alkanes and alkenes, and water soluble constituents such as methanol, butyl acrylate and other solvents stored at the site. Groundwater from selected monitoring wells were exhaustively extracted (base/neutral and acid) and analyzed by GC/MS. Analysis for cations and anions, alkalinity, hydrogen sulfide, metals, and DOC were conducted by Beak Consultants Analytical Services in Brampton, Ontario. Chlorinated alkanes, and alkenes, ethene, ethane, volatile fatty acids, water soluble constituents and GC/MS analysis were conducted by Ralph Dickhout at University of Waterloo, Department of Earth Sciences, Waterloo, Ontario. Jim Gossett of Cornell University, NY, provided confirmatory chlorinated and ethene and ethane analysis as well as hydrogen gas analysis.

Geology The site geology was assessed using continuous coring techniques in selected locations, drillers logs, and downhole geophysical methods. Core material collected during continuous coring operations was subsampled for grain size analysis and F_{oc} determinations (analysis conducted by the University of Waterloo). Hydrogeological data were obtained from the site by monthly measurements of the piezometric level in monitoring wells, well response tests and drawdown responses during pumping.

Aquifer Sediments. The Waterloo Saturated Sand Sampler (WSSS) was used to secure and retrieve aquifer sediments from an area known to have concentrations of PCE (ISRP 5-1). The sediments were for use in microcosms and microbial assessment. Once the WSSS was brought to the surface, the core liner was removed and quickly cut into 60 to 70 cm lengths, capped, and the liner cut lengthwise with a circular saw. One core was not split but was capped, wrapped, placed on dry ice and express-shipped to the University of Tennessee for phospholipid fatty acid analysis. Split cores were immediately placed into an anaerobic glove box and sterile tools were used to pare off the outermost portions of the core. The inner, aseptic core material was collected and distributed into sterile Whirl-Pak bags which were placed in to anaerobic jars. The jars were sealed, then removed and stored on ice for transport from the site to the University of Waterloo.

Enumeration of Microbial Populations. Sulphate-reducing and methanogenic bacteria were enumerated using a three-tube, most probable number (MPN) procedure using a modified (McInerney *et al.*, 1979) Postgate medium (1984). All culture tubes were incubated at room temperature for up to 3 months. Methanogens were enumerated in a Zehnder and Wuhrmann (1979) medium modified by Zeikus *et al.* (1979). Total phospholipids were extracted from frozen subsurface sediments by a modified single phase chloroform-methanol method as previously described (Bobbie & White 1980). Methyl esters of the phospholipids (phospholipid fatty acids, PLFA) were analyzed by capillary GC as described by Bobbie and White (1980) and Guckert *et al.* (1986). Analysis of PLFA has been demonstrated to provide reproducible, quantitative and qualitative information of the total biomass, community structure, and nutritional status of subsurface microorganisms (Balkwill *et al.* 1988).

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[1] This is abridged version of a same titled paper to be published in *In Situ* Bioreclamation. Ed. R. Hinchee, Butterworth Publishers, 1991.

[2] Ibid

Microcosm studies

The microcosms consisted of 20 g (dwt) sediment plus site water, with or without amendments, in sterile 60 mL hypovials. After the addition of sediment, each hypovial was filled to capacity with amended or unamended site water, sealed with a sterile, teflon-lined Tuf-Bond septum (Pierce) and aluminium crimp seal. Amendments included: PCE only, PCE plus methanol, PCE plus acetate, or PCE plus acetate and methanol. The amendments were added to site water at concentrations of 5 mg/L for PCE and 50 mg/L for acetate or methanol; when both primary substrates were present, they were added at a concentration of 25 mg/L each. Control microcosms were similarly constructed as treatment microcosms and consisted of: PCE-H_2O controls containing only PCE in sterile, distilled water; autoclaved/poisoned controls containing PCE;and dissolved oxygen controls containing PCE, sediment, and site water.

Upon removal from the glovebox, the completed microcosms were inverted and placed into argon-filled paint cans equipped with GasPak Plus H_2/CO_2 generator envelopes (BBL). The cans were sealed and incubated at 10C. Periodically a set of microcosms was removed from the incubator, warmed to room temperature, and sacrificed for analysis. Each treatment sample point is the mean result from three replicate microcosms.

RESULTS

Field. The geologic cross section (Figure 2) along transect A-A' (Figure 1) intersects the area of PCE contamination and parallels the NE to SW direction of groundwater flow. The geology is composed of clay till (upper clay) underlain in order by a sand silt unit (upper sand/silt), clay unit (lower clay), layered sand/silt unit (lower sand/silt), and bedrock. The upper clay unit is weathered, and fractured and contains numerous sand and silt lenses and stringers of uncertain lateral extent.

Dissolved chlorinated organics have been detected in groundwater samples collected from monitoring wells installed in the upper sand/silt and upper clay units. Free-phase PCE was obtained from the monitoring well CEL-3 installed in the upper clay. The lower clay unit is very stiff and appears to be a competent aquitard. The lower sand/silt unit appeared to be uncontaminated. The hydraulic conductivity of the upper clay unit was estimated by grain size analysis to be in the range of 10^{-8} to 10^{-9} cm/s. By contrast, the lower sand/silt layer had hydraulic conductivities of 10^{-6} to 10^{-7} cm/s in the northern portion of this unit, and 10^{-5} cm/s in the central area as determined by response tests. Differences in the hydraulic conductivities affect the ratio of vertical to lateral groundwater flow and velocity (Figure 2). Generally, groundwater flow was from NE to SE with a horizontal velocity in the central area of 0.02 to 2 m/y.

Monitoring wells were located within the upper sand/silt and upper clay units at approximate depths of 3 and 7 mbgs. The geochemical results presented focus on samples collected at 7 mbgs monitoring wells because there were more sampling points and greater hydraulic conductivity (and thus groundwater velocity) at this depth. The distribution of PCE, TCE, cDCE, and VC (Figure 3a, b, c, d, respectively) show similar lateral extent. cDCE was found to be the predominant isomer of DCE. Groundwater samples from ISRP 4-1 had detectable concentrations of cDCE (Figure 3c), indicating it has migrated further down-gradient. The additional lateral extent of cDCE, as compared to PCE and TCE, could be attributed to differences in the log K_{ow} of these compounds. The log K_{ow} of PCE and TCE are 2.6 and 2.5, respectively, whereas, the log K_{ow} of cDCE is 1.9. The log K_{ow} of VC (0.9) is the lowest of the chlorinated ethenes and thus would be expected to have a greater lateral distribution. Since VC did not have a greater lateral distribution, it is possible that VC is undergoing an additional transformation step.

We suspect that free-product PCE had migrated along the spur line gravel pack and found at least two points of entry into the aquifer: one centred on PW-1 and CEL-24 and the other on CEL-1 (Figure 3a). Further, distinct biological activities appeared to be associated with each centre of contamination. The samples collected from PW-1 had a higher cDCE concentration (5.540 mg/L) than the concentration of PCE or TCE (0.440 mg/L and 1.165 mg/L, respectively), whereas samples from CEL-1 had similar concentrations of cDCE and PCE (5.813 and 4.376 mg/L, respectively) and a lower TCE concentration (1.654 mg/L). The samples from ISRP 5-1 exhibited a trend similar to that of PW-1, with an elevated cDCE concentration (76.480 mg/L) as compared to either PCE and TCE, which were not detected (< 0.0001 mg/L). The concentration of VC in groundwater samples from ISRP 5-1 (9.712 mg/L) and PW-1 (1.369 mg/L) were higher than in groundwater samples from CEL-1 (0.228 mg/L).

The groundwater sample from CEL-1 had a lower ethene concentration (.020 mg/L) compared to ethene concentrations (Figure 4a) in samples from ISRP 5-1, ISRP 4-1, and PW-1 (0.423 mg/L, 0.152 mg/L, and 0.278 mg/L, respectively). The high ethene concentration in samples from ISRP 4-1, coupled with the lack of other chlorinated ethenes, indicates that ethene has migrated from the source area near ISRP 5-1 and PW-1 (Figure 4a). Ethane was detected only in association with ethene, but at very low concentrations (ISRP 5-1, 0.010 mg/L; PW1, 0.010 mg/L). Methanol was found at this stratigraphic level (Figure 4b) only in groundwater samples from PW1 (810 mg/L) and ISRP 5-1 (5 mg/L), but was also detected in groundwater samples taken from wells located in higher stratigraphic units in the same area (CEL-10, 498 mg/L; ISRP 5-2, 40 mg/L; and ISRP 5-3, 1770 mg/L). Methanol was not detected in groundwater samples taken in the vicinity of CEL-1. Acetate, although more widely distributed than methanol, still appears to originate from around PW-1 and ISRP 5-1 (Figure 4c). It was detected in groundwater samples taken from ISRP 5-1 (430 mg/L) and PW1 (715 mg/L), but not CEL-1. Methane (data not shown) was detected throughout the site and did not appear to be correlated with previously presented parameters. Sulphate concentrations generally decrease in the central area of chlorinated organic contamination at the 3 mbgs level plan map (data not shown). At 7 mbgs sulphate concentrations are low in samples from PW-1 (< 10 mg/L), but are significantly greater in samples from ISRP 5-1 (230 mg/L). Chloride concentrations were elevated in groundwater samples taken from monitoring wells located in the contaminated zones. Elevated chloride levels in groundwater samples could result from dechlorination of PCE and its daughter products. The chloride plume overlaps the chlorinated organic contours and is distributed further down gradient (Figure 4d). The highest chloride concentrations were observed in groundwater samples taken from PW1 and ISRP 5-1 (360 and 380 mg/L, respectively). Chloride concentrations outside the contaminated area where typically in the 10 mg/L range.

Laboratory

Enumeration of microbial population. Viable sulphate-reducing and methanogenic populations were detected in the collected subsurface sediment based upon both culturing and phospholipid analysis. Methanogens were estimated to be less than 40 MPN per gdwt with the various substrates (acetate, 4 MPN; methanol, 21 MPN; H_2-CO_2, 39 MPN). Sulphate reducers are present at approximately 1000 to 3000 MPN per gdwt soil (acetate, 1400 MPN; lactate 3600 MPN).

PLFA analysis (Table 1) of the core material indicated that the microbial community is sparse (1 to 3 x 10^7 bacteria/gdw based on 10 pmole of PLFA = 10^5 bacteria), anaerobic as indicated by the dominance of anaerobic desaturase phospholipids (monoenoic ω7,16 and 18's), predominantly Gram negative (ratio of PLFA to LPS lipid A hydroxy fatty acids), and stressed (cy17:0). Evidence of sulphate-reducing bacteria (SRB) was the presence of short-chain saturated PLFA. The detection of i17:1 and i17:0 PLFA were indicative of *Desulfovibrio*, and 10me16:0 (and no detection of 10Me18:0) PLFA indicate the presence of *Desulfobacter*. The biomass of SRB as estimated by pmole of SRB-PLFA (assuming 10 pmole is approximately 10^5 bacterial cells) was equivalent to SRB estimates by MPN. Isoprenoid ethers, which would indicate methanogens, were not detected at this low density of cells. These data suggest that neither sulphate reducers nor methanogens comprise a significant proportion of the microbial biomass in the sediment.

Microcosm studies. Purging site groundwater to remove residual halocarbons was not entirely successful. Table 2 lists the halocarbon content of the 5 treatment flasks of site groundwater used to prepare the various microcosm treatments. All but the unamended water received 5 mg/L added PCE, but no other halogenated compound. However, residual halocarbon, principally cDCE and excess PCE, remained. Unamended water, for example, was purged for approximately 24 h, but contained 24 mg/L cDCE. Low levels of VC were detected in the purged groundwater containing cDCE. Since VC is a highly volatile compound, we can only explain its presence as resulting from abiotic reactions of residual halocarbons with iron complexes (Vogel *et al.* 1987) or microbial activity may have occurred in the unsterilized groundwater after sampling but prior to analysis. The difference between the halocarbon concentrations in the treatment flasks (Table 2), and day zero of the microcosms (Table 3) is attributed to volatilization from the flask during dispensing of the amended groundwater. However, the concentration of PCE delivered to the microcosms appears to be constant over the microcosm construction period. This is evident in the sterile PCE-H_2O and PCE-soil control microcosms (Figure 5). The construction time difference between the day 0 and day 145 microcosms was approximately one hour, however, the concentration of PCE in these microcosms is relatively stable over the 145 day incubation period. The aquifer sediments did not significantly contribute to the day 0 halocarbon concentrations in the microcosms because sediment samples collected from the control area did not have detectable concentrations of sorbed halocarbons (data not shown).

Microbiologically active microcosms were successfully constructed from the collected subsurface material, as methane evolution and changes in the halocarbon species and concentrations were evident in active microcosm treatments, but not in the PCE-H_2O or the autoclaved/poisoned sterile controls (Figure 5). The decrease in PCE concentration in the autoclaved/poisoned controls may reflect irreversible sorption of PCE to the sediment.

Figure 6 demonstrates biologically mediated transformation of PCE in microcosms amended by PCE plus acetate/methanol. The same general transformation pattern was observed in all active (i.e., nonsterile) microcosms (Table 3). Over time, PCE was dechlorinated to TCE, then cDCE, VC, and finally, in most instances, to ethene. The transformation pattern appears strictly sequential. Small amounts of tDCE and 1,1-DCE were detected in some active microcosms up to day 46, but these were minor in comparison to the cDCE levels encountered. The prevalence of cDCE is in agreement with others (Parsons & Lage, 1985, Scholz-Muramatsu *et al.* 1990). In microcosms that contained initial concentrations of cDCE, its concentration remained unchanged while PCE decreased and TCE increased in concentration. Only when TCE was being depleted did the cDCE concentration rise (Table 3). This pattern held for each successive dechlorination daughter product. The rate of product formation and transformation also slowed as the less chlorinated products appeared.

Microcosms amended with PCE plus methanol and acetate showed more evolved ethene (0.5 mg/L at day 145) than any other amendment (Table 3). By day 145 VC was the sole halogenated compound remaining and was decreasing in concentration. Dechlorination was slowest in the PCE plus methanol treatment with vinyl chloride concentrations still increasing by day 145, whereas in all other treatments (except unamended), VC concentrations were decreasing (Table 3). The unamended treatment was probably exceptional in this regard because of the very large cDCE concentration in these microcosms. It is also notable that methane evolution was delayed in the PCE plus methanol treatment (Table 3) and no ethene was ever detected. This is in contrast to other treatments, in which ethene was present and increasing in concentration from day 83 to day 145. Indeed, in unamended microcosms ethene was detected (at the minimum detection levels) as early as day 12. Further reduction of ethene to ethane was not observed in any of the microcosms (data not shown).

Dechlorination and methane production in both unamended and amended microcosms with only PCE (Table 3) indicate that an electron donor was available in the microcosms without additional methanol or acetate. Chemical analysis of groundwater samples from ISRP 5-1 (obtained near the area from which the core material used in this study was taken) confirmed that both methanol and acetate were present in the area at concentrations from 5 to more than 810 mg/L.

Although methane was evolved in all active microcosms, no correlation between methane production and dechlorination was perceived. The methane concentration reached 41 mg/L in PCE plus acetate amended microcosms at day 145, but dechlorination was more complete in PCE plus acetate and methanol amended microcosms where methane concentration reached 6 mg/L. Dechlorination (and methane evolution) were relatively delayed in PCE plus methanol amended microcosms, but methane concentrations in that treatment were 11 mg/L at day 145.

DISCUSSION

Chlorinated aliphatics have been demonstrated to undergo anaerobic dechlorination in continuous-flow fixed-film reactors (Bouwer & McCarty, 1983, Bouwer & Wright, 1988, Vogel & McCarty, 1985, 1987) in soil (Kleopfer *et al.* 1985), sediment (Barrio-Lage *et al.* 1986, 1987, Parsons *et al.* 1985, Parsons & Lage, 1985), and aquifer microcosms (Parsons *et al.* 1984, Wilson *et al.* 1983, 1986). Although few studies have been conducted on the biotransformation of PCE in the field, many sites contaminated with PCE also have concentrations of dechlorination products in sampled groundwater and aquifer solids. Unfortunately, VC tends to persist in anaerobic environments and is more toxic than the parent compounds.

For anaerobic bioremediation to be a useful remedial method, PCE and TCE must be completely dechlorinated to nonchlorinated products. Few studies have shown the complete dechlorination of chlorinated ethenes. Vogel and McCarty (1985, 1987) have shown the conversion of PCE and VC to CO_2. Freedman and Gossett (1989) studied the conversion of [^{14}C]PCE to [^{14}C]ethene. Their experiments showed insignificant amounts of [^{14}C]CO_2 and [^{14}C]CH_4. They also observed that the rate limiting step was the conversion of VC to ethene, and that the presence of an electron donor was necessary. Methanol was the most effective electron donor. They found that 2-bromoethanesulfonate inhibited the conversion of PCE to ethene, which suggest that methanogens are playing a role in the conversion.

If the dechlorination products of PCE were persisting at our study site then greater downgradient transport of these products would be expected to occur. This is because of two reasons. First, the log K_{ow} value decreases with the removal of a chlorine atom. This results in the dechlorinated products having higher mobility than their more chlorinated predecessor. Second, dechlorination products will form at the leading edge of its predecessor's plume. The good degree of distribution overlap of PCE, TCE, cDCE, and VC at the study site strongly indicates the dechlorination of these compounds.

The predominance of the cDCE (as opposed to the *trans*- or 1,1-DCE isomers) is in agreement with our and other laboratory biotransformation studies of PCE (Barrio-Lage *et al.* 1986, Parsons *et al.* 1984, 1985, Parsons & Lage 1985). Methanol and acetate appears to be promoting PCE biotransformation to ethene. The evidence supporting this conclusion is the strong relationship between PCE, methanol, ethene, and acetate contours originating from the PW1 and ISRP 5-1 monitoring well locations. In contrast, PCE originating from the CEL-1 does not overlap with the methanol, acetate, and ethene plumes.

Contamination of the microcosms with residual halogenated compounds created three complications in the study: (1) the initial PCE levels were not the same in all PCE-containing microcosms; (2) the total concentration of halogenated compounds in the different microcosm treatments was highly varied, although within a set of microcosms (*e.g.*, the "PCE plus methanol" treatment) the initial halocarbon concentration and speciation was constant; and (3) the unamended microcosms, which ideally would be devoid of halogenated compounds, contained very large amounts of cDCE. These complications limit the amount of information gained from the study, but a number of useful results and conclusions were still acquired.

The presence of cDCE in unamended microcosms prevents the unequivocal conclusion that ethene production was the consequence of vinyl chloride dechlorination because we had no active microcosms devoid of ethene. Ethene was certainly a metabolic product because it was not formed in sterile controls, but ethene is synthesized naturally by some soil microorganisms (Alexander 1977). However, it is likely that ethene was the final product of the PCE transformation sequence in the sediment, as Freedman and Gossett (1989) found in their enrichment cultures. If ethene is assumed to be the daughter product of VC, then the early appearance of this nonchlorinated daughter product in unamended microcosms was probably related to the absence of PCE and TCE. In these microcosms, the reaction sequence started at cDCE, and although the bulk of the reductive activity was directed towards VC production, some dechlorination of VC to ethene also occurred. Despite its early appearance, ethene did not accumulate in the unamended microcosms (0.06 mg/L by day 145) nearly to the extent that it did in other ethene-positive treatments (PCE only, 0.34 mg/L; PCE plus acetate, 0.11 mg/L; PCE plus acetate and methanol, 0.51 mg/L; all after day 145), again suggesting that throughout the entire period of monitoring, most dechlorinating activity in the unamended microcosms was directed toward the large cDCE mass. This evidence, and the observation of strict sequential dechlorination of the halogenated compounds in the microcosms, indicate that reduction order, although biologically driven, was dictated by the reduction potential of the halocarbon parent-daughter product pair in question.

The microcosm experiments corroborate field evidence that PCE dechlorination is biologically-driven, and ethene is probably the final, nonchlorinated product of the sequence. Although methane was produced in all active microcosms, there was no correlation between methane evolution and dechlorination. The treatments could be ranked as follows, in terms of methane production: PCE plus acetate > PCE plus methanol > PCE only > PCE plus methanol and acetate > unamended. However, if ranked in terms of dechlorination over 145 days (indicated by final ethene concentration: initial halocarbon concentration), the ranking was quite different: PCE plus methanol and acetate > PCE only > PCE plus acetate > unamended > PCE plus methanol.

The mechanism or the microorganisms responsible for dechlorination of PCE to ethene is not clear. Few studies have examined which anaerobic microorganisms are responsible for reductive dechlorination. Methanogenic enrichment cultures (utilizing acetate) have been shown to dechlorinate aliphatics (Bouwer & McCarty 1983). Galli and McCarty (1989) have shown that a *Clostridium* sp. was able to biotransform 1,1,1-trichloroethane forming volatile acids (*e.g.*, acetate). Egli *et al.* (1987) have demonstrated that chlorinated ethanes can be dechlorinated by *Desulfobacter autotrophicum*. Bagley and Gossett (1990) found that PCE was dechlorinated to TCE and cDCE in sulphate-reducing enrichment cultures, but that this activity decreased over time. In contrast Fathepure *et al.* (1987) found that *Desulfovibrio desulfuricans* and two species of *Clostridium* did not produce significant quantities of TCE from PCE. The authors also tested the ability of four acetate-utilizing methanogens to dechlorinate PCE. *Methanosarcina acetivorans* and *Methanothrix* did not produce significant quantities of TCE from PCE, but the dechlorination rate of *Methanosarcina* sp. and *M. mazei* cultures paralleled methane production, and maximum yields of TCE were obtained with methanol as opposed to acetate.

In our study, the lack of a relationship between methane production and dechlorination, and the marked differences in microcosm behaviour depending upon treatment (for example, the methanol- versus acetate-amendments) suggest that: (a) activity of methanogenic bacteria was not necessarily mediating the observed dechlorination reactions; and (b) the provision of the different electron donors enriched different segments of the microbial population native to the subsurface sediment.

These points and the low population densities of methanogens and SRB in the subsurface sediments suggest that other organisms may be involved in the dechlorination reactions observed *in situ*. The detection of acetate in groundwater samples containing concentrations of methanol hints that acetogens may play an important role in the dechlorination of PCE to ethene. We hypothesize that methanol is serving as a substrate for acetogenic microorganisms that may be responsible for dechlorination of PCE at the study site.

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Table 1: PFLA Core Sediment Analysis[1]

PFLA	Sample Location in Core	
	Top	Bottom
12:0	1.25	0.58
i14:0	0.05	0.54
14:0	5.81	3.75
i15:0	5.87	5.33
a15:0	2.76	2.46
15:0	3.54	3.32
i16:0	0.68	0.40
16:1w7c	16.21	26.16
16:1w5c	1.06	1.72
16:0	30.73	18.26
i17:1	0.00	0.79
10me16:0	0.88	0.96
i17:0	0.31	0.44
a17:0	0.08	0.38
cy17:0	9.01	15.49
17:0	0.21	0.83
18:3w6	1.31	0.00
18:2w6	0.00	0.00
i18:/3w3	0.00	0.00
18:1w9c	7.47	9.21
18:1w7c	5.98	2.41
18:0	6.79	6.23
10me18:0	0.00	0.00
br19:1	0.00	0.75
cy19:0	0.00	0.00
20:1w9c	0.00	0.00
Total	100.00	100.00
pmole/gdws	29.9	11.7
LPS Lipid-A OH-FA Analysis		
3OH12:0	0.00	0.00
2OH12:0	100.00	0.00
2OH14:0	0.00	0.00
Total	100.00	100.00
pmole/gdws	0.13	0.00

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[1] Nomenclature: Total number of carbon atoms: number of double bonds with position of double bond closest to the ω end with geometry 'c' for *cis*, 't' for *trans*; 'i', 'a', and 'br' refer to iso, anteiso, and methyl-branching, respectively. Methy-branching from the Δ end is indicated by its position followed by Me and the total number of carbon atoms; Cyclopropyl fatty acids are designated as ' cy'.

Table 2: Halocarbon concentrations in purged site water after addition of PCE and substrate amendments prior to distribution to microcosms (mg/L)

Amendment	PCE	TCE	cDCE	tDCE	1,1-DCE	VC
unamended	0.36	0	24.14	0	0	0.26
PCE	2.53	0.08	3.47	0	0	0.08
PCE + methanol	7.95	0	9.46	0.002	0.001	0.42
PCE + acetate	13.92	0	0	0	0	0
PCE + methanol/acetate	11.87	0	0.67	0	0	0.003

PCE added: 5 mg/L (3.1 µL per L), except to unamended

TABLE 3: Biotransformation Products (mg/L) of PCE by Treatment (Standard Deviation)

Treatment	Day	PCE	TCE	cDCE	VC	Ethene	Methane
PCE	0	0.372 (0.104)	0.145 (0.077)	2.350 (0.272)	0.034 (0.003)	0 (0)	0.027 (0.005)
	12	0.041 (0.059)	0.339 (0.052)	2.122 (0.321)	0.185 (0.027)	0 (0)	0.190 (0.027)
	25	0.004 (0.002)	0.029 (0.004)	2.436 (0.479)	0.279 (0.039)	0 (0)	0.491 (0.017)
	46	0.006 (0.011)	0.002 (0.004)	1.469 (0.144)	1.167 (0.071)	0 (0)	0.800 (0.123)
	83	0 (0)	0 (0)	0 (0)	1.689 (0.057)	0.092 (0.005)	4.258 (0.715)
	145	n.d	0 (0)	0 (0)	7.290 (0.321)	0.061 (0.017)	2.624 (0.543)
PCE + Methanol	0	1.965 (0.800)	0.004 (0.006)	5.116 (0.337)	0.021 (0.007)	0 (0)	0.005 (0.005)
	12	1.019 (1.015)	0.265 (0.277)	6.015 (0.925)	0.060 (0.001)	0 (0)	0.010 (0.003)
	25	0.050 (0.006)	0.012 (0.003)	5.845 (0.954)	0.060 (0.011)	0 (0)	0.094 (0.045)
	46	0.040 (0.015)	0.010 (0.010)	4.772 (0.229)	0.177 (0.22)	0 (0)	0.185 (0.123)
	83	0 (0)	0 (0)	4.380 (0.832)	1.074 (0.033)	0 (0)	1.751 (0.519)
	145	n.d	0 (0)	1.250 (0.5[illegible]1)	2.434 (0.147)	0 (0)	11.083(1.708)
PCE + Acetate	0	0.672 (0.076)	0.003 (0.003)	0.676 (0.283)	0.002 (0.003)	0 (0)	0.008 (0.001)
	12	0.076 (0.025)	0.237 (0.037)	0.650 (0.069)	0.001 (0.002)	0 (0)	0.063 (0.005)
	25	0.024 (0.004)	0.023 (0.006)	1.095 (0.156)	0.031 (0.005)	0 (0)	0.756 (0.050)
	46	0.020 (0.015)	0.007 (0.002)	0.863 (0.058)	0.201 (0.036)	0 (0)	3.145 (0.190)
	83	0 (0)	0 (0)	0 (0)	1.055 (0.038)	0.033 (0.006)	23.818(7.919)
	145	n.d	0 (0)	0 (0)	0.813 (0.051)	0.109 (0.023)	40.916(8.633)
PCE + Methanol and Acetate	0	1.641 (1.054)	0.085 (0.057)	0.627 (0.014)	0.007 (0.005)	0 (0)	0.008 (0.001)
	12	0.012 (0.002)	0.186 (0.026)	1.752 (0.162)	0.098 (0.005)	0 (0)	0.076 (0.014)
	25	0.004 (0.001)	0.013 (0.002)	1.685 (0.040)	0.229 (0.003)	0 (0)	0.655 (0.067)
	46	0 (0)	0.002 (0.004)	0.559 (0.073)	1.093 (0.026)	0 (0)	1.617 (0.101)
	83	0 (0)	0 (0)	0 (0)	1.188 (0.038)	0.238 (0.133)	4.074 (1.983)
	145	n.d	0 (0)	0 (0)	0.175 (0.153)	0.512 (0.082)	6.033 (0.187)

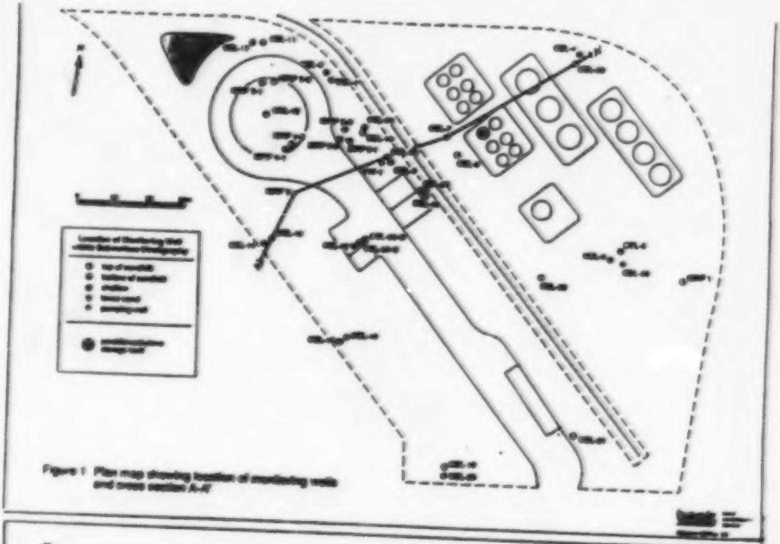


Figure 1 Plan map showing location of monitoring wells and cross section A-A'

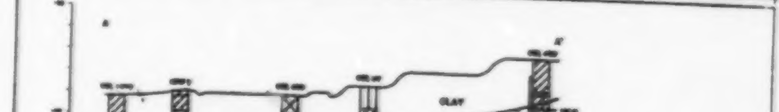

A
A'
CLAY
SILTY CLAY
CLAY
LAYERED SANDSILT

Figure 2 Hydrostratigraphic cross section A-A' showing subsurface geology, hydraulic head equipotentials, and direction of groundwater flow

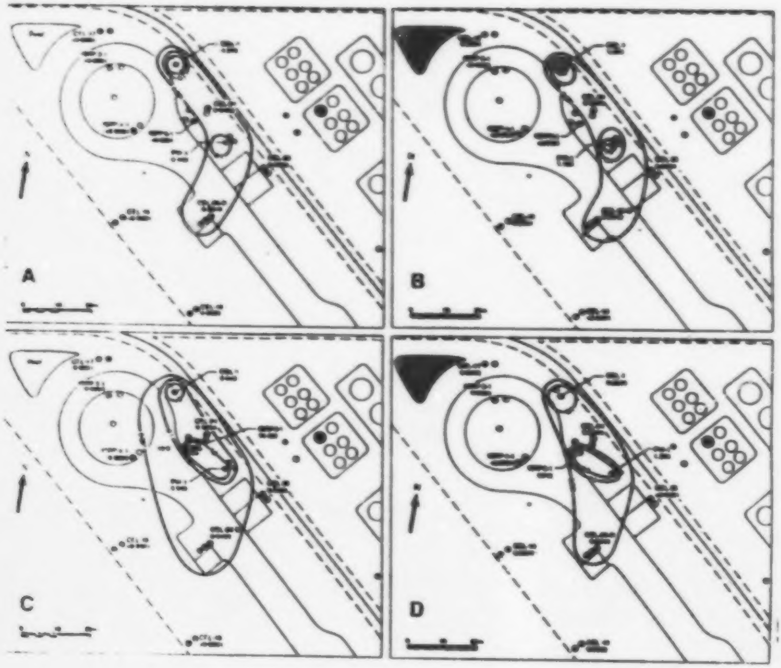


Figure 3 Contours of (A) PCE (mg/L), (B) TCE (mg/L), (C) cDCE (mg/L), and (D) VC (mg/L) in the bottom of the sand/silt at a depth of approximately 7 m bgs

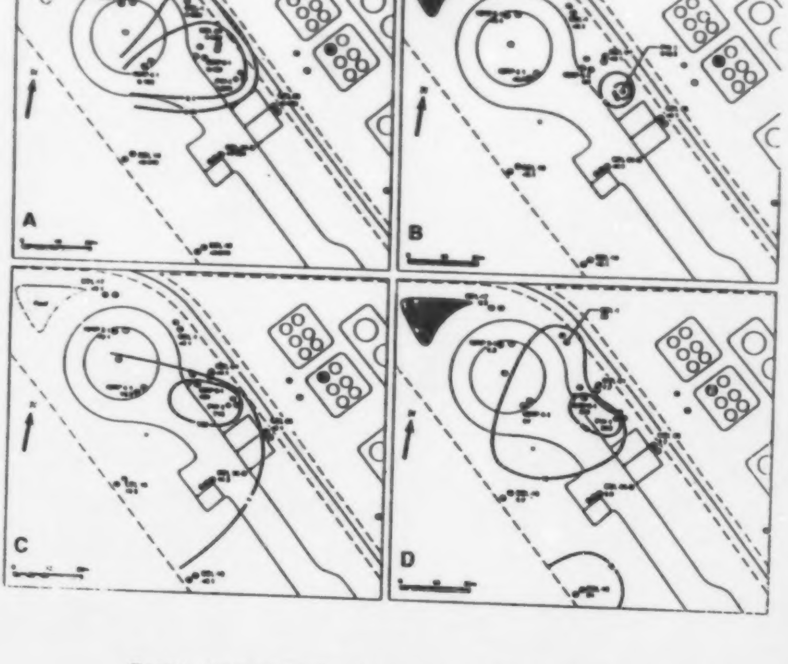
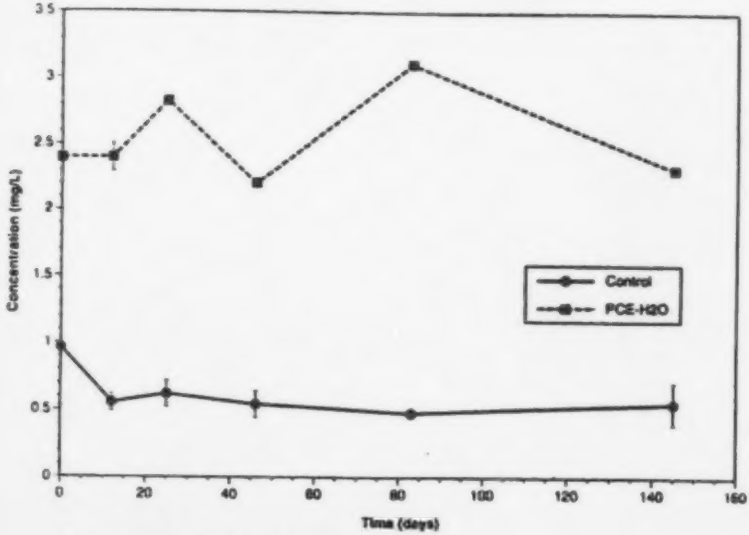


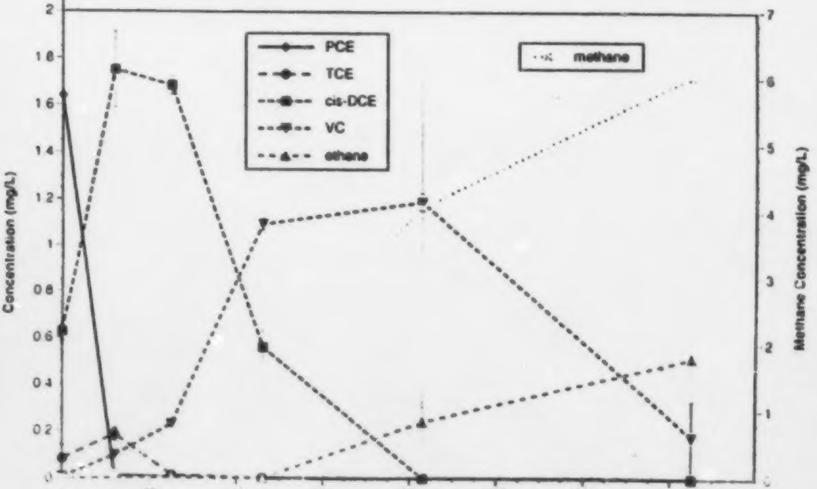
Figure 4 Contours of (A) ethene (mg/L), (B) methanol (mg/L), (C) acetic acid (mg/L), and (D) chloride (mg/L) in the bottom of the sand/silt at a depth of approximately 7 m bgs

Figure 5: PCE Controls*



* Other dechlorination products not detected

Figure 6: PCE + methanol + acetate amendment



VOLUME II

SESSION F

PREVENTION, TREATMENT AND REMEDIATION

POSTER PRESENTATIONS

FP1

CHARACTERIZATION AND BIOTECHNICAL USES OF THE EXTRACELLULAR EMULSIFYING AGENT PRODUCED BY *PSEUDOMONAS AERUGINOSA*

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Biosurfactants are compounds produced on microbial cell surfaces or excreted extracellularly, which contain both hydrophilic and hydrophobic portions. Due to their amphipathic nature, surfactants aggregate at an interface, causing a reduction in surface and interfacial tensions. Since biosurfactants and bioemulsifiers both exhibit emulsification properties, bioemulsifiers are often categorized with biosurfactants, although emulsifiers may not lower surface tension.

Petroleum refineries produce large amounts of oily wastes, such as complex hydrocarbons. These hydrocarbons and some halogenated compounds are serious environmental pollutants, which may cause public health and ecological concerns due to their persistence and toxicity to biological systems. Land farming is an acceptable method for the disposal of oily sludge (Berwick and Stafford, 1985; Shailubhai, 1986). This technique involves spreading oily sludge onto soil, and providing optimal conditions to allow mineralization of hydrocarbons by soil microorganisms.

Hydrophobic compounds bind to soil particles, and are difficult to remove or degrade. Efficient degradation requires that hydrocarbons are solubilized before being degraded by microbial cells (Stucki and Alexander, 1987; Thomas *et al.*, 1986). For some hydrophobic compounds, the rate of mineralization is governed by desorption of hydrocarbons from soil (Mihelcic and Luthy, 1988a and 1988b). It is expected that surfactants can increase the surface area of hydrophobic materials, thereby increasing the water solubility. The addition of biosurfactants to the soil may enhance hydrocarbon dispersion and increase microbial degradation (Van Dyke *et al.* 1991).

Many microorganisms are able to produce surface active substances. We have been studying the characteristics of a biosurfactant produced by *Pseudomonas aeruginosa* UG2. Strain UG2 was isolated initially in our laboratory from oil contaminated soil (MacElwee *et al.*, 1990). Other researchers have shown that *P. aeruginosa* is able to produce rhamnolipid surfactants of varying structure. Jarvis and Johnson (1949), and Edward and Hayashi (1965) determined the rhamnolipid produced by *P. aeruginosa* is composed of 2 units of L-rhamnose and 2 units of β-hydroxydecanoic acid linked to the C1 position. Hirayama and Kato (1982) and Parra *et al.* (1989) determined that their *P. aeruginosa* strains produced 2 types of rhamnolipid. The first type contained 2 units each of L-rhamnose and β-hydroxydecanoic acid, while the second was similar except that it contained only one unit of L-rhamnose. *Pseudomonas* sp. DSM 2874 (Syldatk *et al.*, 1985) was found to produce 4 different types of rhamnolipids, containing either one or two units each of L-rhamnose and β-hydroxydecanoic acid. Yamaguchi *et al.* (1976) isolated a *Pseudomonas* strain that produced 2 rhamnolipids similar to that of Parra *et al.* (1989), except both glycolipids also contain 2-decenoic acid at the C2 position.

We have carried out some structural characterization of the partially purified *P. aeruginosa* UG2 biosurfactant. Analysis by HPLC and GC showed that the UG2 biosurfactant does contain L-rhamnose as the only sugar. Analysis by GC-MS indicated the presence of β-hydroxydecanoic acid and 2-decenoic acid. Therefore, we propose the structure of the *P. aeruginosa* UG2 rhamnolipid biosurfactant may be similar to those reported by Yamaguchi *et al.* (1976). Currently NMR analysis of UG2 rhamnolipids is being performed, and should provide further information on the structural arrangement of these components.

The biosurfactant produced by *P. aeruginosa* UG2 was previously found to solubilize hexachlorobiphenyl significantly in soil slurries Berg *et al.* (1990). We carried out additional partitioning studies to further investigate the ability of the UG2 biosurfactant to solubilize other hydrophobic contaminants. These studies involved spiking small amounts of soil with ^{14}C-labelled compounds, and washing the soil with surfactant solutions. The amount of ^{14}C-compound that was removed from soil into the aqueous phase was measured by scintillation counting.

In the first experiment, several hydrophobic compounds were tested in soil that contains a high amount of organic matter. The compounds tested were pyridine, naphthalene, anthracene, phenanthrene, fluorene, 2,5,2',5'- tetrachlorobiphenyl and 2,4,5,3',4',5'-hexachlorobiphenyl. All these compounds except pyridine are hydrophobic. As pyridine is water soluble, it served as a control. Partially purified, freeze dried UG2 biosurfactant was tested over the concentration range of 0.1 to 5 mg/ml.

Pyridine recovery was high (>80%) at all biosurfactant concentrations. In general, the % recovery of the more hydrophobic compounds in the aqueous phase was found to increase as UG2 biosurfactant concentration increased. However, the extent of recovery varied with the hydrocarbons. The recovery of naphthalene was 70% at 5 g biosurfactant/l, while that of anthracene, fluorene and phenanthrene were about 30-40%. The recovery of hexachlorobiphenyl was also high at 70%, while that tetrachlorobiphenyl was 40%.

These results are important because they show that all the tested hydrophobic compounds may be solubilized to varying extent by the UG2 biosurfactant. The basis for the variability in the degree of solubilization is not known. This variability is unlikely to be related to the compounds' aqueous solubilities since one of the more water-soluble (naphthalene) and one of the least water-soluble (hexachlorobiphenyl) hydrocarbons were recovered to about the same extent. More likely, the variability was dependent on factors such as soil type and content, the extent of binding (or adsorption) of the hydrophobic compounds to the soil matrix, the prevailing environmental conditions, or the nature and type of interactions between the biosurfactant and the hydrophobic substances. These are important questions that should be addressed in further studies.

In a second partitioning experiment, a sandy loam soil was used, which has a lower amount of organic matter. Again, pyridine recovery in the aqueous phase was greater than 80% at all biosurfactant concentrations tested. At 5 g biosurfactant/l, the recoveries of naphthalene, anthracene, fluorene and phenanthrene from the sandy soil were all approximately 10% higher than those from the silt loam soil. The % recovery was about 80% for naphthalene, and about 40-50% for anthracene, fluorene and phenanthrene. On the other hand, the recovery of hexachlorobiphenyl from the sandy soil was about 10% lower than that from the silt loam soil, while the recovery of tetrachlorobiphenyl was about 10 % higher. The % solubilization of both hexachlorobiphenyl and tetrachlorobiphenyl was very similar throughout the concentration range of UG2 biosurfactant tested. This experiment clearly showed that soil type does have an effect on the ability of the UG2 biosurfactant to dislodge hydrophobic compounds from soils. Higher levels of organic matter may bind hydrophobic compounds more firmly, making removal more difficult.

In a third partitioning experiment, the ability to solubilize hydrocarbons in soil slurries was compared between the anionic chemical surfactant SDS and the anionic UG2 biosurfactant. Using the Conestogo silt loam soil, the % recoveries of naphthalene and anthracene were about the same for SDS and UG2 surfactants. The % recoveries of phenanthrene, fluorene, tetrachlorobiphenyl and hexachlorobiphenyl were clearly higher using the UG2 biosurfactant. The same experiment was repeated using the sandy loam soil. The % recovery of naphthalene was approximately the same using SDS and UG2 surfactant, but the recoveries of anthracene, phenanthrene and fluorene were about 10% higher using the UG2 biosurfactant than using SDS. Recoveries of hexachlorobiphenyl and tetrachlorobiphenyl using the UG2 biosurfactant were over 20% higher than using SDS. These experiments demonstrated that the UG2 biosurfactant is superior to SDS in the partitioning of hydrophobic compounds from soil into the aqueous phase.

Studies are in progress to investigate the effect of UG2 biosurfactant on microbial degradation of hydrocarbons in soil. Solubilization and degradation experiments may show that biosurfactants can be used to enhance recovery of pollutants from contaminated soil.

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FP2

Investigation of Ontario Mixed Layer Mica-Vermiculite as Potential Landfill Liner Material and Adsorbent of Organic and Inorganic Pollutants

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Clay minerals in clay soils which are commonly used as landfill liners, must have a low permeability and high filtering ability. Although all types of locally available clays are used, the most suitable type of clays possess the following characteristics: high cation exchange capacity, large specific surface area and the presence of surface functional groups (hydroxylated edges, broken chemical bonds, sites with organic or inorganic ions).

Glaciolacustrine clays which are widespread in southern Ontario often contain illite and chlorite. These clays generally have low cation exchange capacities (C.E.C.) and low specific surface areas. The more suitable Champlain Sea clays which are used in Quebec as landfill liners and substrata, have a better C.E.C. when compared to the glaciolacustrine clays (50 meq/100 g versus 20 meq/100 g). Smectite group clays and vermiculite have a specific surface area which is an order of magnitude larger than that of illite and chlorite. Vermiculite has one of the highest C.E.C.'s among the clay minerals, and would appear to be a desirable component for landfill liners.

Although commercial grade deposits of vermiculite are presently unknown in Ontario, an occurrence of mixed layer mica-vermiculite in southern Ontario has been documented by MacKinnon et al (1990). This site was chosen for study, in particular since a large stockpile of the material was present, which could be readily bulk sampled (Figure 1). The deposit occurs 13 km south of Perth, approximately 350 km from Toronto, and 80 km from Ottawa. The deposit has been previously assessed to determine the viability of using it as a source of expanded vermiculite (which is used as an insulator, an absorbent of fertilizers, etc.).

Samples of vermiculite from the Stanleyville deposit as well as the hydrothermally clay altered host rock were studied by petrography, x-ray diffraction, electron microprobe analysis and scanning electron microscopy.

In addition, selected samples were evaluated to determine their C.E.C.'s and their ability to retain heavy metals when subjected to leaching tests using landfill leachate solutions.

RESULTS

Chemical Composition and Mineralogy

Electron microprobe analysis suggests that the 'micas' at Stanleyville range in composition from serpentine to phlogopite. The low Al content of the Stanleyville 'micas' is notable when compared to commercial vermiculite deposits (Figure 2). Individual grains from Stanleyville samples show a wide variation in K/Mg and K/Al ratios, as confirmed by microprobe and SEM analysis.

XRD analysis was subsequently performed on samples collected from the open pit and trenches. Some samples were treated with KCl, NaCl, $MgCl_2$ or NH_4-acetate, in addition to heating and ethylene glycol treatments.

The results of this work suggest that much of the coarser material previously classed as vermiculite in Stanleyville is in fact a mixture of phlogopite and lizardite, contained within a matrix of aliettite, smectite, talc and vermiculite, with minor amounts of hydrobiotite. Aliettite, present in all samples, is a regularly interstratified mixed-layer clay mineral in which talc and saponite are the constituent layers. A number of XRD profiles illustrating the behaviour of the Stanleyville aliettite and vermiculite when subjected to various treatments are shown in Figures 2, 3 and 4.

In view of the lower than anticipated vermiculite content, the samples from Stanleyville were expected to have a low cation exchange capacity. Predicted C.E.C.'s for the samples analyzed based on XRD and mineralogical analysis ranged from 15 meq/100 g to 37 meq/100 g.

Soil Chemistry

Cation exchange and heavy metal retention tests were conducted on a variety of samples. The C.E.C.'s were determined using batch equilibrium tests and by the silver-thiourea method. Results indicated that exchangeable Na^+ and K^+ were low (<0.5 meq/100 g); and exchangeable Ca^{2+} and Mg^{2+} moderate to high (1 to 17 meq/100 g). Total C.E.C.'s were in the order of 7 to 19 meq/100 g. Grinding of several fractions did not produce a significant increase in C.E.C.

Heavy metal retention tests were conducted using spiked solutions from an actual landfill site. The composition of the leachate is shown in Table 1.

TABLE 1. LEACHATE CHARACTERIZATION*
(mg/L or ppm)

PHYSICAL		ORGANICS		ANIONS		CATIONS		HEAVY METALS	
pH	7.06	Oil and Grease	17	NH_4	192	Na^+	144.9	Pb^{2+}	35.4
Conductivity (u ohm/cm)	8803			NO_2^-, NO_3^-	<0.1	K^+	74.9	Zn^{2+}	38.3
Alkalinity	4340			Cl^-	1515	Ca^{2+}	23.48	Cr^{3+}	28.4
				SO_4^{2-}	27.1	Mg^{2+}	21.7	Cd^{2+}	1.2

* - unspiked

The results of the heavy metal retention studies with low heavy metal contents demonstrated that retention was high, being greater than 90% in all cases. Two of the soils with higher C.E.C. were tested using spiked leachate with high heavy metal concentrations (Pb^{2+} up to 6380 ppm, Zn^{2+} up to 2400 ppm). It was noted that the retention of the Pb^{2+} and Zn^{2+} increased with the initial cation concentration used and was maximized at about 500 ppm. At high concentrations, the % adsorbed is lower (<50%), as indicated for one example shown in Table 2. It was also noted that the maximum amount of these heavy metals retained could exceed the C.E.C. of the soil. Retention of up to 24 meq/100 g of Zn^{2+} and 36 meq/100 g of Pb^{2+} was achieved over the range of heavy metal concentrations studied. An increase in pH of the effluent solution was noted after the tests (initial pH = 1-2, final pH = 2-4).

The specific surface area of the soils are moderately high, ranging from 90 m^2/g to 206 m^2/g. Determinations of permeability on one sample compacted wet of optimum moisture content (14.4%) indicated an average value of 1.2×10^{-7} cm/sec.

TABLE 2. PARTIAL RESULTS OF HEAVY METAL RETENTION (HIGH CONCENTRATIONS)
(Soil No. 10, C.E.C. = 16.50 meq/100g)

Pb^{2+}				Zn^{2+}				Pb^{2+}, Zn^{2+} or (Pb^{2+}+Zn^{2+}) Adsorbed (meq/100g)
Influent (ppm)	Effluent (ppm)	Adsorbed (ppm)	% Adsorbed	Influent (ppm)	Effluent (ppm)	Adsorbed (ppm)	% Adsorbed	
500	60	440	88.0	-	-	-	-	4.25
1000	320	680	68.0	-	-	-	-	6.56
3000	1750	1250	41.7	-	-	-	-	12.07
6000	3850	2150	35.8	-	-	-	-	20.75
-	-	-	-	600	232	368	61.3	11.26
-	-	-	-	1200	730	470	39.2	14.38
-	-	-	-	2400	1620	780	32.5	23.86
500	250	250	50.0	150	79	71	47.3	4.58
1000	610	390	39.0	300	182	118	39.3	7.37
2000	1050	950	47.5	600	364	236	39.3	16.39
4000	3075	925	23.1	1200	775	425	35.4	21.93
"8000" (3400)	3000	400	11.8	"2400" (2350)	1300	1050	44.7	35.98
-*	0*	-*	-*	-*	0.2*	-*	-*	-*

* - Test blank
() - Actual concentration

CONCLUSIONS

Results to date suggest the Stanleyville deposit is composed of phlogopite, lizardite, aliettite, smectite, talc, vermiculite and minor hydrobiotite. Due to the lower than expected vermiculite content, the C.E.C.'s were low; however, the total adsorbed cation (Pb^{2+}, Zn^{2+}, Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}) retention can exceed the C.E.C. of the soil. Given the low pH values of the effluent solutions, precipitation of the heavy metals is unlikely to explain this observation. Secondly, there appears to be a strong retention of Ca^{2+} and Mg^{2+} which contributes significantly to the high C.E.C. The specific surface areas of the soils are moderately high, and selected compacted soils returned low permeability results.

Given these characteristics, as well as the ability of the minerals to create a moderately alkaline pH in the aqueous environment, the deposit at Perth may constitute a speciality resource for the remediation of certain toxic pollutants. Future investigations being considered relate to identifying the mechanism of contaminant retention, determining the organic pollutant retention capabilities, and the probability of increasing the C.E.C. of the stockpiled material via clay mixing processes.

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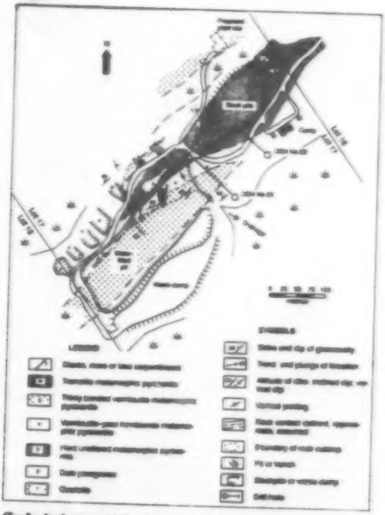
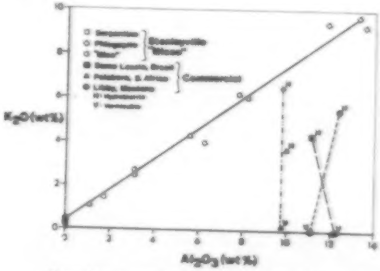
Figure 1



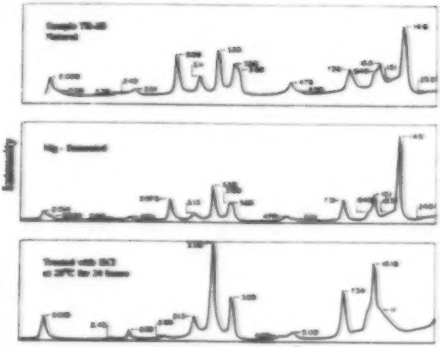
Geological map of the Olympus Mines Ltd. property (after Guillet 1962).

Figure 2



Potassium versus aluminum plot for "Mica" grains from Stanleyville and selected commercial deposits.

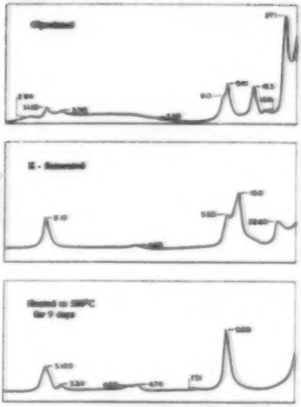
Figure 3 (a)



D spacing, Values in Å

XRD PROFILE - VERMICULITE

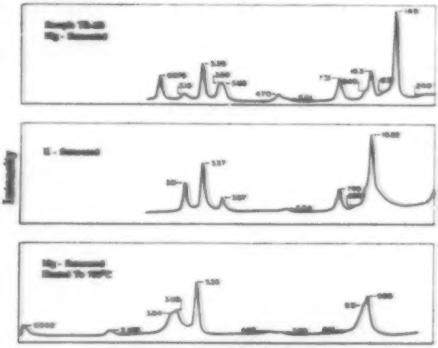
Figure 4 (a)



D spacing, Values in Å

XRD PROFILE - ALIETTITE

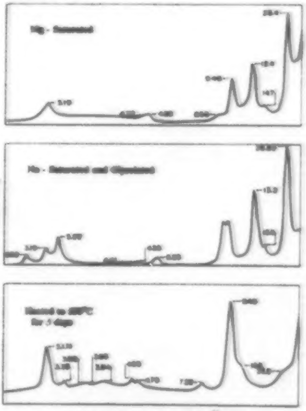
Figure 3 (b)



D spacing, Values in Å

XRD PROFILE - VERMICULITE

Figure 4 (b)



D spacing, Values in Å

XRD PROFILE - ALIETTITE

Figure 5 Heavy Metal Retention

Figure 5 (a)

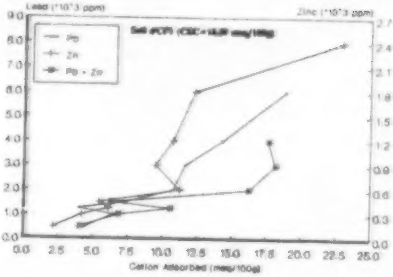


Figure 5 (b)

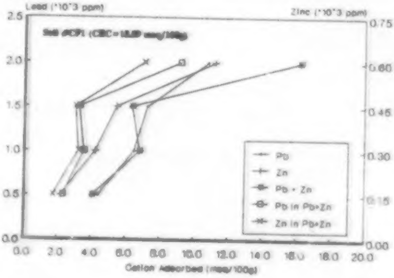


Figure 5 (c)

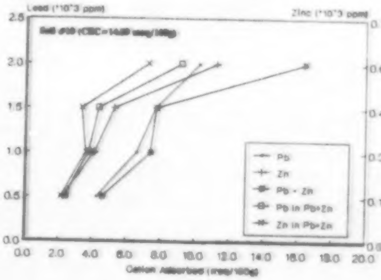


Figure 5 (d)

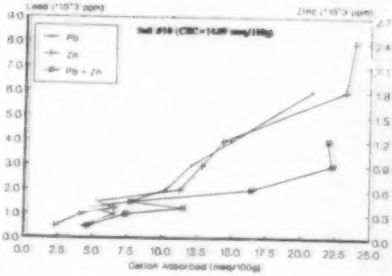


Figure 5 (e)

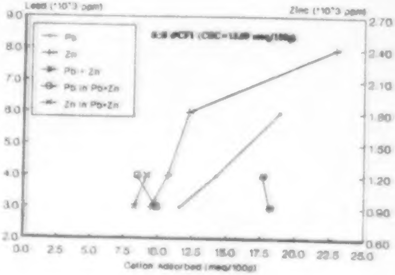
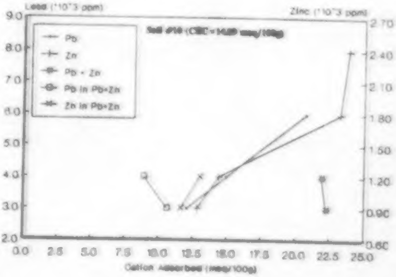


Figure 5 (f)



FP3

FLASH PHOTOLYSIS/HPLC METHOD FOR DETERMINING THE SEQUENCE OF PHOTOCHEMICAL REACTIONS[†]

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A new method involving the use of flash photolysis followed by rapid high performance liquid chromatography analysis is applied to the examination of the photodegradation of phenol (I) and 4-chlorophenol (II) in undegassed aqueous solution (10^{-4} - 10^{-3} M). Analysis of the solution following a single flash (direct photolysis) indicates that *p*-benzoquinone (III) is the only major photoproduct from the photolysis of either I or II. After several flashes other products appear, namely hydroquinone (IV) and 2-hydroxy-*p*-benzoquinone (V), which are known photoproducts from the direct photolysis of III. This was confirmed by a study of III subjected to a single flash. In other experiments, solutions of II containing varying amounts of H_2O_2 were subjected to flash photolysis. When the ratio of $[H_2O_2]$ to II exceeded 20:1, the product distribution changed such that 4-chlorocatechol (VI) is the major photoproduct with a smaller amount of IV and 1,2,4,-trihydroxybenzene (VII). The results will be discussed and mechanisms proposed.

INTRODUCTION

Although a number of water purification techniques are available, the oxidation of aqueous organic pollutants is an attractive method because of its high efficiency and simplicity (5,6). The oxidation products are usually low molecular-weight oxygenated compounds that are easily biodegradable. In the past decade or so, the potential use of the photooxidation of organic pollutants in the presence of H_2O_2 has aroused the considerable interest in the environmental community.

[†] Most of the work presented in this paper has been published, is in press or has been submitted (see references 1-4).

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Phenols and chlorophenols are common pollutants found in effluents from pulp mills and in the production of fungicides and herbicides. Since previous studies have yielded a rather confusing and incomplete picture concerning the photolysis of phenols and chlorophenols in model and natural systems, we have undertaken a detailed study of the sequence of products formed in both direct photolysis and photolysis mediated by hydrogen peroxide.

To address the problems encountered in previous investigations, we have developed a method utilizing the technique of flash photolysis; however, instead of using the conventional configuration where subsequent reactions are followed by detecting the optical absorption of transients, we have employed HPLC detection to detect and identify moderately-lived intermediates. With this approach we can obtain a significant fraction of conversion with a single flash and thus avoid the possibility of photolysis of intermediates. Also by using multiple flashes, we can follow the sequence of intermediates in the reaction. This technique is limited to the detection of intermediates with lifetimes greater than ~15 min, *i.e.*, the time required to complete an HPLC run.

We have used phenol (I) and 4-chlorophenol (II) as model compounds for testing the method, since the photoreaction of these compounds has been studied using conventional approaches (7,8), which have yielded a much more complex series of photoproducts.

RESULTS AND DISCUSSION

In the first set of experiments, undegassed solutions of I and II were subjected to 1 - 30 flashes (45 J) and analyzed within 2 min. by HPLC. After only one flash *p*-benzoquinone (III) is the only photoproduct. Its identity was confirmed by isolation and analysis by FTIR, ^1H FTNMR, UV and mass spectrometry. After 5 - 10 flashes, new compounds begin to appear: hydroquinone (IV) and 2-hydroxy-*p*-benzoquinone (V), which are known photoproducts from the photolysis of III. This was confirmed by flashing solutions of III in a separate series of experiments.

After 20 - 30 flashes, traces of 1,2,4-trihydroxybenzene (VII) are observed in the case of the photolysis of I and both VII and 4-chlorocatechol (VI) in the case of the photolysis of II.

In a second set of experiments we have examined the distribution of photoproducts from the flash photolysis of II as a function of the ratio of the concentration of H_2O_2 to that of II, kept at 9.6×10^{-4} M. At concentration ratios between 0.6 and 20, the amount of III formed decreases, while the amounts of IV and VI increase significantly. This shows a clear changeover of products from those found in direct photolysis to those found in the hydrogen peroxide mediated photolysis.

It has been known for a long time that hydrogen peroxide photolyses to produce ·OH radicals, which react with aromatic compounds by adding to the ring to produce hydroxylated products. Thus, the observation that VI is the major product observed after a single flash is quite understandable. Some ·OH radicals also displace chlorine atoms in II since IV and V are significant products.

In a final set of experiments, the direct photolysis quantum yield was found to be 0.13 for I and 0.24 for II using a broadband technique based on the photolysis of III as an actinometer (quantum yield = 0.47).

CONCLUSIONS

1. When studied at low concentration, where bimolecular reaction steps are slow, the photochemistry of phenol and 4-chlorophenol is particularly simple, yielding *p*-benzoquinone as the major photoproduct.

2. In the case of II, as the ratio $[H_2O_2]/[II]$ increases, the photoreaction mechanism changes from direct photolysis (where III is the major direct photoproduct) to H_2O_2 mediated photolysis (where VI is the major photoproduct).

Finally, we conclude that the new technique of flash photolysis/HPLC is very effective in elucidating the detailed reaction sequence of aqueous photochemical reactions of environmental interest.

ACKNOWLEDGEMENTS

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FP4

DEVELOPMENT OF A HEPATIC MICRONUCLEUS ASSAY IN FISH, C.D. Metcalfe and C.R. Williams, Environmental and Resource Studies Program, Trent University, Peterborough, Ontario K9J 7B8.

An *in vivo* hepatic micronucleus assay with rainbow trout is being developed to test for the genotoxic effects of aquatic contaminants. An assay protocol has been developed in which proliferation of hepatocytes in the trout liver is stimulated by a regenerative response after exposure to allyl formate (AF). Two protocols have been tested in which trout are exposed to the clastogen before or after exposure to AF. Both protocols give a positive response with the indirect-acting clastogen, diethylnitrosamine (DEN). The direct-acting clastogens, ethyl methanesulphonate and mitomycin C, have been tested using the protocol in which AF exposure occurs first, and both of these compounds gave a positive response in this assay. Tests are continuing with other genotoxic chemicals, including the PAH compound, benzo(a)pyrene.

FP5

EPR SPIN TRAPPING DETECTION OF SHORT-LIVED RADICAL INTERMEDIATES IN THE DIRECT PHOTOLYSIS OF 4-CHLOROPHENOL IN AERATED AQUEOUS SOLUTION[†]

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The photolysis of 4-chlorophenol (I) in aqueous solution (pH = 6.5 to 10.5) in the presence of the spin trap 5,5-dimethylpyrroline-N-oxide (DMPO) results in the formation of at least five distinct EPR spectra. We have identified three of these as arising from the DMPO spin adducts of: the hydrogen atom [or a hydrated electron plus later protonation] (spectrum A), an aryl radical [probably the *p*-hydroxyphenyl radical] (spectrum B) and the ·OH radical (spectrum C). Spectrum D probably arises from a decomposition product of one or more of the spin adducts, and spectrum E is that of the *p*-benzosemiquinone anion. By examining EPR spectra after various times of uv irradiation and determining the time course of the growth of each spectrum, we have established that spectra A and B appear immediately on initiation of the photolysis. In contrast, the growth of spectrum C is sigmoidal, indicating that it arises from a secondary product. We present a mechanism, based on the primary radicals detected, that accounts for the photoconversion of I to *p*-benzoquinone (II).

INTRODUCTION

The direct photolysis of organic pollutants (mostly aromatic) in the natural environment is stimulated by solar radiation in the range 290-400 nm. In addition, artificial photolysis, using uv lamps with a large fraction of their output below 300 nm, is gaining interest as a commercial process for the removal of these organic pollutants. Unfortunately, very little is known about the detailed mechanism of the direct photolysis of most aromatic organic pollutants in aqueous solution.

[†] The results described in this abstract are to be published as a paper in the Journal of Photochemistry and Photobiology.

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Chlorophenols are found as important pollutants in effluents from pulp and paper mills, as well as in the production of pesticides and herbicides. Some information is available concerning the longer-lived photoproducts. Boule *et al.* (1) found that the reaction is non-specific, giving *p*-benzoquinone, hydroquinone, biphenyls and polyphenolylic oligomers. Recently we have reexamined this photochemical reaction under more dilute conditions using a flash photolysis/HPLC technique (2) and find that *p*-benzoquinone (II) is the only major photoproduct from the direct photolysis of 4-chlorophenol (I) in aqueous solution. In spite of this knowledge, relatively little is known about the detailed mechanism leading to the known stable photoproducts.

The technique of spin trapping, with electron paramagnetic resonance (EPR) detection of free radical intermediates (3), has proven to be valuable in the study of the mechanisms of photolysis reactions. For example, it has been shown that ·OH radicals are produced as a primary product in the photolysis of *p*-benzoquinone (II) in aqueous solution (4). We have recently used this technique to determine the rate constants for the reaction of ·OH radicals with various chlorophenols (5a) and halobenzene derivatives (5b) in aqueous solution.

The purpose of the present work was to investigate the mechanism of the formation of II from the photolysis of I using the spin-trapping technique with EPR spectroscopy.

RESULTS AND DISCUSSION

When I is photolyzed by uv light in the EPR cavity in the presence of DMPO at pH 8.5, several EPR spectra can be detected. A computer reconstruction reveals that there are at least four distinct spectra, which we have been able to assign to the following radicals: (A) the hydrogen atom DMPO spin adduct; (B) an aryl (phenyl type) DMPO spin adduct; (C) the ·OH radical DMPO spin adduct; (D) an unidentified radical with a single interacting nitrogen nucleus, which we suspect to be a decomposition product of one of the DMPO spin adducts.

Most of the spectral features are well reproduced by the simulated EPR, and we have found that we can fit almost all the EPR spectra under various conditions by simulations made up of varying proportions of the four base EPR spectra. In addition, under some conditions (especially at higher pH) the EPR spectrum of the *p*-benzosemiquinone anion radical is observed.

As the uv irradiation progresses, spectrum C increases in relation to the others. This indicates that the ·OH spin adduct is likely formed in a secondary reaction. As further confirmation we have examined the time course of the rise of the EPR signal for four field positions characteristic of each spectral species. Spectra A and B rise immediately on initiation of the uv irradiation, indicating that these probably arise from primary radicals; however, spectrum C exhibits a sigmoidal rise, indicating that it arises from a secondary radical. We propose that spectrum C arises from the generation of ·OH radicals from the photolysis of II produced from the photolysis of I. Although spectrum D overlaps a line from spectrum A, we believe that species D also arises from a secondary photochemical process.

As a control we have carried out a series of experiments in which we have irradiated phenol (III) in the presence of DMPO under the same conditions as for the photolysis of I. We have found that the contribution from species B is much less in the photolysis of III as compared to I. We interpret these observations to indicate that the carbon-centered radical (B), produced in the photolysis of I, arises primarily from the homolytic fission of the carbon-chlorine bond of I. The fact that hydrogen atoms (or hydrated electron followed by protonation) are generated from the photolysis of both I and III indicates that they arise from the photochemistry of the phenol chromophore.

We observed previously (2) that, on bubbling with a gas stream containing progressively lower partial pressures of oxygen, the yield of II dropped off significantly, indicating that the photoreaction of I probably involves oxygen as a reactant. We find that the EPR spectrum shows a much stronger contribution from spectrum C (the ·OH spin adduct) in aerated solutions as compared with the EPR spectrum in nitrogen bubbled solutions. This is expected if more II is formed in the aerated solution, as compared with the nitrogen-bubbled solution.

Although the overall appearance of the EPR spectra change with increasing pH, the component EPR spectra do not, except at high pH where the EPR spectrum (Spectrum E) of the *p*-benzosemiquinone anion is detected. The generation of this species is independent of the presence of DMPO.

Our observations lead us to the conclusion that the only primary free radicals produced from the photolysis of I are hydrogen atoms (or hydrated electrons followed by protonation) and an aryl (probably *p*-hydroxyphenyl) radical. The control experiments with phenol indicate that the hydrogen atom arises from the phenol entity.

Ononye *et al.* (4) have shown that the excited state of II attacks water to produce *p*-benzosemiquinone and hydroxyl radicals with a high quantum yield (~0.5). In the present studies, the generation of *p*-benzosemiquinone anion radicals from the photolysis of I was detected by EPR. Hence our present observation that the DMPO-OH spin adduct arises from a secondary photolysis reaction, and the detection of the *p*-benzosemiquinone anion in photolyzed solutions of I, supports the proposal that most of the ·OH radicals are generated from the secondary photolysis of II.

CONCLUSIONS

Our spin-trapping EPR experiments have permitted a much more detailed description of the mechanism of the photolysis of I and of III on route to formation of III. Further details will be presented in the poster.

ACKNOWLEDGEMENTS

This work was supported by research grants from the Ontario Ministry of the Environment and the Natural Sciences and Engineering Research Council, for which we give grateful thanks.

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VOLUME II

SESSION G

TECHNOLOGIES/BIOTECHNOLOGY

VERBAL PRESENTATIONS

G1

A COMPARISON OF ELECTROTHERMAL VAPORIZATION AND DIRECT SAMPLE INSERTION FOR THE ANALYSIS SOLIDS BY ICP-AES

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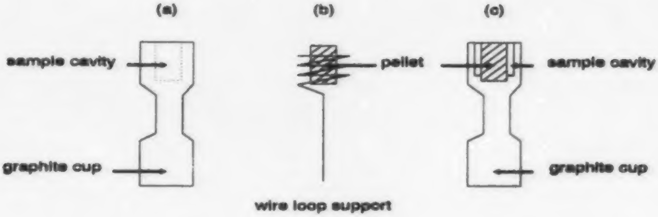
It is important to appreciate that most of the inhabited world is solid. While we have an active interest in water and air, we live on the land. To monitor our environment, we must then monitor the land and it's products. Even the air and water exist in an equilibrium with the land. In this equilibrium, the land surface is often the major contributor of environmental contaminants. With this simplification in mind, one can appreciate that most environmental samples are solid or, if liquid, very far from being pure water. This has led us to concentrate our elemental analysis research on the development of new solid sample analysis methodologies. In our work on sample introduction methodologies we have come to appreciate the difference between academic and "real world" analytical environments. An appreciation of the real world can lead to an alteration in the way in which the analytical chemistry must be done. Our work with Direct Sample Insertion (DSI) analysis techniques for inductively coupled plasma atomic emission spectrometry (ICP-AES) started in the early nineteen eighties. The DSI technique requires the use of a sample carrying probe as illustrated in Figure 1.

The sample is placed in or on the probe, and then inserted into the plasma along the central axis. A number of apparent advantages accrue, foremost among them, 100% sample delivery. If the delivery is over a short length of time, then improved detection limits can be realized (1). In fact, we were even able to realize sub 1% relative standard deviations when the system was automated and liquid samples were inserted with a wire loop probe (2). There can also be some negative aspects to using a sample carrying probe: [1] The probe can break down and contribute to the spectrum, and [2] the sample can react with the probe. None-the-less, the promise of 100% sample delivery is very attractive. As we will see, however, the delivery of 100% of a real sample may not be as desirable as one would originally expect. This, in turn, leads us to consider other ways in which we might achieve the desired analytical goals.

FIGURE 1


(a)
(b)
(c)
sample cavity
pellet
sample cavity
graphite cup
graphite cup
wire loop support

DSI Analysis of Geological Materials

Our initial work with DSI systems and liquid samples was very successful. Detection limits were improved by factors of roughly 10-100 and precision of the order of 0.5 - 1% was obtained with pure water standards. We immediately began an aggressive assault on solid samples. A study indicated that estuarine sediments were of considerable interest to the MOE as they constituted a significant fraction of the total work load in both numbers and difficulty of converting to a liquid form suitable for analysis by conventional ICP sample introductions systems.

CONVENTIONAL DSI

Our first approach involved the use of conventional probes, slightly modified d.c. arc electrodes. This work indicated that we were going to have troubles with detection limits. Unlike our convenient solid standards, dilute oxides in graphite, real geological samples were going to be a problem. Geological samples have a matrix, usually some form of Si, which is resistant to low power chemical and physical attack. The traditional ICP-AES methodology commonly involves digestion with HF for a significant length of time. The DSI-ICP-AES approach involved the use of high temperatures, approximately 2000 degrees Centigrade. Given the excellent excitation characteristics of the plasma, one might expect much higher temperatures; however, one must keep in mind that the ICP, while an excellent *spectral excitation source*, is not a particularly good *heater*. It is usually operated at about 1 kW, roughly the power of an automobile block heater, and the majority of the power goes to maintaining the plasma, rather than heating the probe. The result is that geological Si based samples usually melt to form a glass type bead which only slowly breaks down. Volatile elements emerge quickly but their signals are highly erratic due to the volcanic effect of the matrix. To avoid the formation of beads, the sample could be diluted in graphite. This led to unsatisfactory detection limits.

PELLET DSI

In an attempt to increase sample mass and yet dilute the sample, we tried a radical approach, the use of graphite pellets (3)as illustrated in Figure 1 (b). Common sense indicated that one could insert only a limited size probe into the ICP. To obtain optimal heating, we simply eliminated the graphite cup which we considered to be an unnecessary heat sink. This arrangement allowed sample masses approximately one order of magnitude larger than that which was possible with conventional probes. A secondary, but very important benefit, was the improvement in precision obtained, from 50% rsd to 8% rsd. A number of facts emerged as we studied DSI-ICP-AES. The first was that excellent detection limits, of the order of 10 ppb, could be obtained for ideal standards. Work with the MOE using ICP-MS also showed excellent results (6).

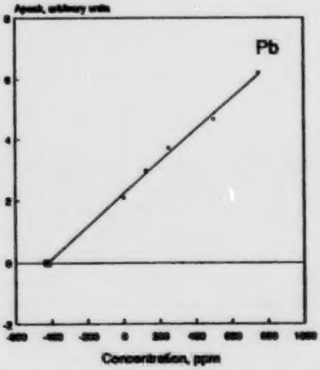
Experimentation with geological standards was extremely informative although disappointing. In short, visual observations served to illustrate the effect that the massive release of Si was having on the plasma. The gaseous Si was clearly disrupting the excitation zone and changing excitation conditions. Only the volatile elements, which emerged before the Si phase, could be analyzed.

PELLET-CUP PROBES

The final stage of the DSI system is presented in Figure 1 (c). A pellet is inserted inside a specially machined graphite cup. The cup directs all vapors upwards ensuring that the plasma is minimally perturbed and that analyte is concentrated in the viewing zone of the plasma. The analyte remains diluted in a pellet providing all the previously discussed advantages. Gases escaping from the pellet move up the space between the inner cup wall and the outer wall of pellet (4,5).

This arrangement allows the additional of chemical additives which can cause the breakdown of the matrix as well as the formation of more volatile analyte species. In our work, AgCl was found to be superior. In some cases it was found that the use of internal standards or standard additions provided superior analytical performance as indicated in Figure 2.

FIGURE 2



PELLET-ETV-ICP

Even before the DSI work above was finished, we had begun work with a pellet ETV-ICP-AES system (7). The rationale behind the pellet approach was identical to that which inspired the original pellet DSI-ICP-AES work: Dilution provides better performance and higher masses provide better detection limits and better precision.

The ETV device used is a modified Perkin-Elmer HGA-2200 graphite furnace. The modification includes the replacement of the original graphite contact rings with home-made brass ones, the construction of a brass "sample holder" and a Pyrex glass chamber, and the use of O-rings for sealing.

Pellets were made of oxides of volatile elements (As, Cd, Hg, Mn, Pb and Zn) are run first to characterize the system. The preparation of pellets includes mixing single element oxide powder with graphite powder, weighing and pressing the mixture. For a batch preparation of five pellets, the process takes about 15 to 20 minutes. The pellet is then put to the notch of the "sample holder" with a pair of tweezers. It goes through a drying cycle at 100^0 C for 2 seconds and charring cycle at 200^0 C for 1 second before it goes on to a vaporization cycle. The drying and charring cycle are necessary to eliminate the moisture and the gas in the pellet. At the vaporization step (1250^0 C, 5.0 seconds), the pellet is heated to incandescence and the analyte is vaporized. The vapor is carried to the plasma by an argon carrier gas. The transient atomic emission signals are usually narrow, well-defined peaks for the volatile elements studied.

A compromise carrier gas flow rate must be used for multielement analysis . The precisions (RSD 3-8% peak heights) are good for solid sample analysis. Linear calibration curves with a range of two to three orders of magnitude were established for Cd, Pb and Zn. The improvement factors in detection limits are 6 to 100 and 30 to 50 respectively in comparison to pellet-DSI and routine liquid sample nebulization .

For reference botanical samples, grinding (10 to 15 minutes in a mortar) is needed if the sample particles are too big. The preparation steps of pellets from these samples are similar to those for single element oxides except that the sample to graphite ratio is kept at 1 to 9 (w/w). Larger ratios result in poor signals or breaking of the pellet. Higher temperatures and longer periods are needed in the drying and charring steps to get rid of the organic matrix of the sample (Drying: 300^0 C, 60 sec; Charring: 400^0 C, 120 sec). The analyte concentrations in these samples are read directly from the calibration curves established with single element oxides. For the two elements (Pb and Zn) monitored, it is found that some of the results have good accuracy, while others do not. The most interesting feature is that the precision in the vegetation samples is quite good, intimating that matrix matched standards or standard additions might provide good accuracy.

Table I: Analysis of MOE botanical samples

(concentration in ppm)

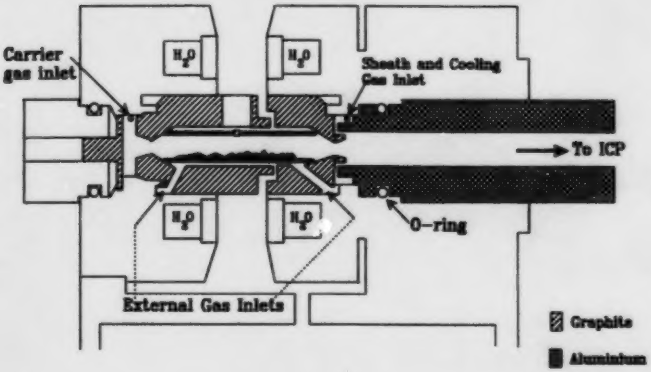
	Pb		**Zn**	
Sample type	**Found**	**MOE**	**Found**	**MOE**
V85-1	10+/-1	19+/-2.0	370+/-12	140+/-11
White birch	3.2+/-0.2	4	370+/-5	200
Norway maple	39+/-1	95	39+/-2	39

In conclusion, this system provides good precisions, improved detection limits and easy calibration using single element oxides. The procedure is simple and fast (10 minutes grinding, 15 minutes pellet preparation). The system is suitable for quick screening of large numbers of vegetation samples for volatile elements. Better results may be possible using more demanding methodologies such as standard additions or internal standards.

LESSONS LEARNED AND BEYOND.

The pellet DSI work has demonstrated that it is possible to analyze even very difficult samples with the DSI technique. The indications are that the same is true for pellet ETV. Unfortunately, when analyzing more difficult samples, the methodologies involved, standard additions and internal standards, may have to be accompanied with a chemical treatment as was done in our latter DSI work. This is unfortunate because it is very inconvenient to use these methodologies with solid materials. They are time consuming, difficult to automate and may introduce additional errors through contamination, particularly with the addition of matrix modifying chemicals. We believe that we must find convenient ways to break down the sample while it is in the solid form. The method should preferably not require solid handling and, ideally, will eliminate the need for the standard additions or internal standards methodology. With this in mind we have built an ETV solid sample introduction system which is specifically tailored to allow gases to be used as reactants to break down the sample. The system is illustrated in Figure 3.

FIGURE 3



The system is most unique in one aspect, it provides a sheathing and "cooling" gas to mix with the gaseous effluent from the furnace. The sheathing gas will keep the analyte from condensing on the wall of the "after burner" tubing while the cooling gas is designed to cause turbulent mixing inside the after burner. Mixing should produce aggregates which will survive the transport to the plasma.

The chemistries possible are quite interesting. For example, gaseous halocarbons (Freon, carbon tetrachloride) can be introduced. On heating, highly reactive radical halides will be formed. These radicals could convert the sample to volatile halides which are vaporized much more easily. Even more interesting, it may be possible to operate the system in a "stop flow" mode. This should concentrate the analyte and allow sufficient time for slower chemical reactions to take place. The after burner also allows some opportunity for chemistry. The introduction of oxygen, for example, would encourage the rapid formation of oxide aggregates, which are quite stable and have higher transport efficiencies than the corresponding halides.

CONCLUSION

We have learned that we are on the right track. The solution to the problem seems to be a more chemical approach, albeit gas phase, rather than a straight physical approach.

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G2

AN INTERRUPTED-FLOW MICROWAVE DIGESTION SYSTEM FOR ENVIRONMENTAL SAMPLE PREPARATION.

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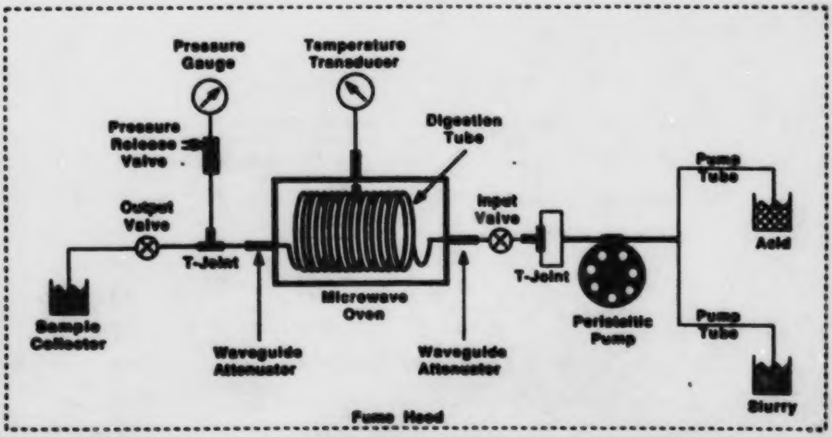
In our laboratory we have worked for the last several years developing a microwave digestion system specifically designed to enhance throughput in the laboratory. The system is dramatically different from conventional microwave systems in that it uses a tube rather than a bomb or open vessel as the sample container. The configuration is illustrated in Figure 1.

FIGURE 1.


Pressure Gauge
Temperature Transducer
Pressure Release Valve
Digestion Tube
Output Valve
Input Valve
Pump Tube
Acid
T-Joint
T-Joint
Microwave Oven
Sample Collector
Peristaltic Pump
Pump Tube
Waveguide Attenuator
Waveguide Attenuator
Slurry
Fume Hood

Sample is prepared in slurry form and then pumped through the tube into the microwave cavity. A conventional "kitchen" microwave oven is used. The tubing becomes a closed vessel when the valves are closed. Microwave energy is then applied for a period as short as two minutes. At the end of the two minute period, the tubing is allowed to cool for one minute and then the pressure is brought to atmospheric level by slowly opening the exhaust valve. The solution is then pumped into a container (or directly to an instrument) while a wash solution follows. The wash solution is then treated for approximately the same length of time. Results obtained from two NBS materials are presented in Table I.

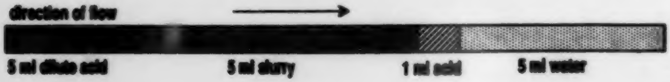
Analysis of NBS Orchard Leaves and Bovine Liver

	Percent Recovery	
Element	**Orchard Leaves**	**Bovine Liver**
Al	29	35
Ba	89	50
Cu	92	100
Fe	90	107
Mg	100	111
Pb		97
Zn	100	98

They are generally quite good, with the exception of Al and Ba, which we discussed at length previously (1990 Technology Transfer Conference). They can be determined either by using extended digestion times or correction factors.

There are several ideas for improvement which resulted from our experiments with this first design. The first was the use of what one could call a segmented plug approach to the distribution of solutions in the tube. We have always been concerned about the escape of materials on the fringes of the acid plug. These would result in analytical errors and also leave solid material which could result in memory effects as well as mechanical degradation of the valves. The solution has been to precede and follow the analyte/slurry plug with a water and then an acid plug. This means that any particles must escape through the acid plug, an unlikely occurrence since this will be a high concentration zone. The configuration is illustrated in Figure 2. An additional improvement has been implemented, a drop in volume from 50 to 25 ml. The system has been tested with NBS Orchard Leaves and results are similar to those which we obtained previously (Table I).

FIGURE 2

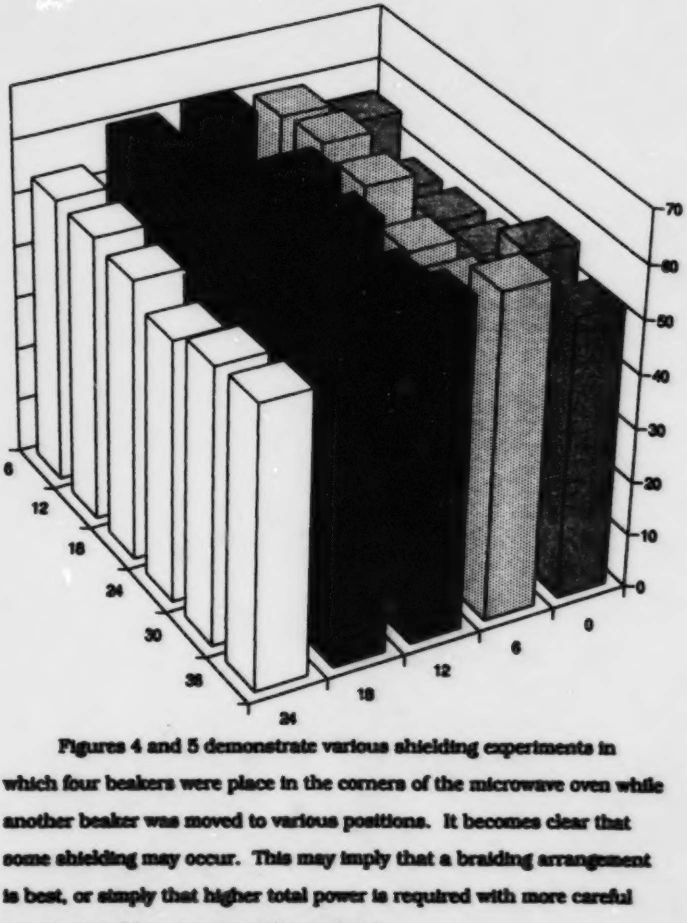


We have apparently eliminated memory effects by using an acid wash and rinse cycle. While this solves the analytical problems, it does bring up a question of throughput advantage. Considerable throughput is lost if the system is digesting only 50% of the time. To overcome this problem, we have been investigating the possibility of a multitube approach. In theory, a two tube system would have a throughput of approximately one sample every two minutes, while a four tube system would have a throughput of one sample every 1 minute. In the last case, the throughput would closely match the throughput of ICP spectrometer systems, however one must not forget that cooling and deaeration would require additional processing along the way, although they need not change the throughput since they could be done in-line.

It is critical that one appreciate that two types of "kitchen" microwave ovens are available at this time. Those with carrousels and those with "spinners" at the top. Carrousel systems deliver power to only a small portion of the oven. The systems work because the material is brought through flux for uniform exposures by the rotating carrousel. This type of arrangement is unsuitable for our type of work, since only a small portion of the coil would be exposed. For this reason, spinner based systems must be used. One then must be concerned about the uniformity of flux inside the oven. To study what might happen in a spinner microwave oven, a series of power distribution experiments were conducted by placing beakers of a fixed volume of water inside a microwave oven. The power was turned on for a fixed length of time, and the change in temperature was used to obtain a measure of the power delivered to an aqueous sample. The data for a single beaker is presented in Figure 3. The vertical axis refers to relative power transferred as indicated by a change in temperature. The other two axes are physical dimensions from one corner. In essence, the "x and y" correspond to the floor of the oven.

Figure 1 indicates a roughly uniform distribution, however, it is interesting to consider what might happen when two coils were placed in the microwave, with one coil on or beside the other. One might then be concerned about shielding effects.

FIGURE 3



Figures 4 and 5 demonstrate various shielding experiments in which four beakers were place in the corners of the microwave oven while another beaker was moved to various positions. It becomes clear that some shielding may occur. This may imply that a braiding arrangement is best, or simply that higher total power is required with more careful monitoring of the pressure within each tube.

FIGURE 4

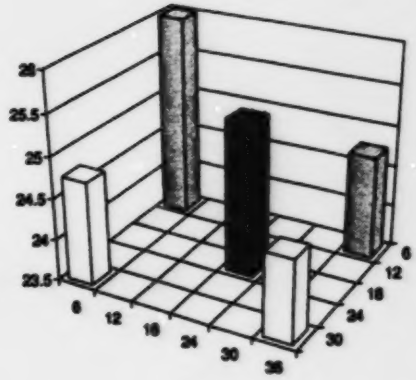


FIGURE 5

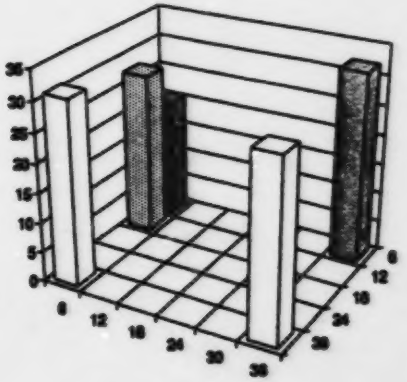


Figure 1 has been simplified somewhat. The present system actually incorporates feedback between the pressure transducer and the power input, thereby minimizing the potential for overpressures and damage to the equipment. When the pressure threshold is exceeded, power is cut to the system until the pressure is reduced to the threshold level. Only extremely rapidly changing pressure levels could now cause damage to the system. This would most probably be caused by using the wrong chemistry on a given sample type, an operator error.

Work continues towards the development of a fully automated system. We will discuss our work towards a "particle proof" valve at the conference.

G3

DEVELOPMENT OF NEW CAPILLARY GC COLUMNS FOR DETERMINATION OF ORGANICS IN ENVIRONMENTAL SAMPLES. Thomas O. Tiernan*, John H. Garrett and Joseph G. Solch, Wright State University, Department of Chemistry, Dayton, Ohio 45435, U.S.A.

A multidimensional computer model has been developed which predicts the functional group composition of stationary phase coatings used in bonded-phase capillary GC columns which will yield optimum separations of selected mixtures of organic compounds. Among the variable parameters incorporated in this model are the temperature program, the head pressure, the column length, the column film thickness, and functional group interactions within the bonded phase. The model ultimately yields functional group capacity factors from which retention time data for separations of selected compounds are calculated for various stationary phase compositions. On the basis of these predictions, the optimum stationary phase is identified and synthesized, and a capillary column is coated with this phase and tested experimentally to evaluate its separation characteristics. The application of the model for predicting the separations of the entire set of the 2,3,7,8-chlorine substituted polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) isomers will be described. In addition, use of the model to predict separations of a set of volatile organic compounds on a series of commercially available columns of different lengths will be demonstrated. The performance of capillary columns prepared by J & W Scientific, our collaborator in this work, on the basis of the model predictions for both of these applications, will be discussed.

FLOW INJECTION PRECONCENTRATION COMBINED WITH DIRECT SAMPLE INSERTION FOR INDUCTIVELY COUPLED PLASMA SPECTROMETRY

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INTRODUCTION

The Inductively Coupled Plasma (ICP) has established an enviable performance record as a source for both atomic emission spectrometry (AES) and mass spectrometry (MS). While matrix effects in ICP-AES are only moderate, it lacks the sub part-per-billion (ppb) detection limits of ICP/MS. On the other hand, ICP/MS suffers from a wide variety of matrix effects [1] which can affect the accuracy of the system. In our laboratory we have experimented with Direct Sample Insertion (DSI) [2] for liquid sample analysis by ICP-AES and ICP/MS. While detection limit advantages are gained with DSI in both AES and MS, DSI-ICP/MS offers the additional advantage of a significant reduction in matrix effects by eliminating the solvent from the sample introduction process [2].

Flow Injection (FI) has been used extensively in configurations commonly called Flow Injection Analysis (FIA) systems [3], and more recently as an approach to extending the capabilities of atomic spectrometry [4]. FI preconcentration offers two important benefits for ICP spectrometry. The first is the preconcentration advantage, generally between one and two orders of magnitude [5-8] . The second advantage arises from the separation of the analytes from interfering matrix constituents. Samples which have undergone the FI preconcentration treatment emerge from the system in the same matrix, namely, that of the eluant. This has advantages for ICP spectrometry, particularly ICP/MS, which is more sensitive to matrix effects than ICP-AES.

One loses a great deal of the advantage of preconcentrating the sample if a significant fraction does not reach the plasma. The low transport efficiency (between 1-5%) of most nebulizer/spray chamber combinations indicates that a special advantage for FI-ICP spectrometry may be gained by using DSI, which provides a sample introduction efficiency of 100%. While previous liquid DSI-ICP-AES and DSI-ICP/MS work in our laboratory was oriented towards the use of wire loops [2,9], there have been several recent reports in the literature that either a thin-walled thin-stemmed graphite cup or a deep undercut electrode give excellent performance with liquid samples [10,11]. These configurations reduce cup mass and facilitate rapid heat transfer to the sample, resulting in narrower, more intense peaks. In our previous report [12] we discussed both the development of special graphite probes for FI-DSI-ICP-AES and the experimental aspects of the method.

In this paper we have addressed the question of the expected "multiplicative effect". It would seem that the preconcentration factor of the FI front end could be almost directly multiplied by the detection limit improvement of DSI-ICP. Since both advantages are significant, about a factor of 10, the combination of the two should provide a stunning improvement, of about two orders of magnitude.

RESULTS AND DISCUSSION

The operating parameters for the flow injection system and the DSI system were optimized separately, as there was no reason to expect any interaction between the two subsystems. The Chelex-100 ion exchange resin columns were optimized with respect to length and inner diameter. "Optimal" in this case was determined to be the column that gave the highest intensity signal in the smallest time window for a fixed sample volume without exceeding the loading capacity of the column. The other operating parameters that were varied include sample loading rate, pH of the buffer, acid strength and elution flow rate. These experiments were normally conducted by running the eluant directly into a nebulizer/spray chamber system.

The precision of determinations at the 5 ppb level (about 100 times the detection limit with clean blanks) using peak integration for the three elements averaged 4% RSD using manual drying of the eluant into a cup. Although this precision is quite good, there is potential for improvement since the DSI system has previously exhibited precisions for liquid work of about 1% [9] when automated.

By collecting small fractions of eluant, it was determined that a 5.0 mL injection volume eluted in approximately 160 µL providing a preconcentration factor of 30, typical of many of the systems described above. Detection limit improvements ranging from x10 to x100 (element specific) have been reported [8] for DSI alone. In Table 1 we have presented detection limits for DSI obtained independently of the FI system. One would then expect that the product of the DSI Improvement Factor and FI Preconcentration Factor would produce detection limit improvements of the magnitudes shown in Table 1. The performance data obtained are given in Table 2. The thin walled cup detection limits of Table 1 were obtained with a slightly different optical arrangement (viewing height and lens position) than that used for the final set of experiments which provided the data in Table 2. Nevertheless, the observed multiplicative effect is certainly of the same order as that predicted.

Table 1. FI-DSI-ICP-AES Performance Expectations

Element	Nebulizer Detection Limit (ppb)	DSI Thin Cup Detection Limit (ppb)	DSI Improvement Factor	FI Preconcn. Factor	Expected Improvement Factor
Pb	30	0.9	30	30	900
Zn	80	0.6	130	30	3900
Cu	8	0.9	9	30	270

Table 2. FI-DSI-ICP-AES Performance Data

Element	Nebulizer Detection Limit (ppb)	Ideal Blank Detection Limit (ppb)	Improvement Factor	Real Blank Detection Limit (ppb)	Improvement Factor
Pb	30	0.05	600	0.04	700
Zn	80	0.07	1200	1	80
Cu	8	0.06	140	0.2	40

As the relatively high nebulizer detection limits in Table 2 reveal, the spectrometer could be considered somewhat sub optimal. Several nebulizers (Meinhard and Légère) imported from a conventional spectrometer provided the solution detection limits presented when used with this system, yet these nebulizers performed up to factory specifications on a newer system, usually providing detection limits about an order magnitude better. Since the purpose of the experiments was to establish the general validity of the multiplicative effect, we are extremely pleased with our results. It is however unfortunate that the optics had not been brought up to optimal at the time of these experiments. None-the-less, detection limits in the 50 ppt range are encouraging at this stage.

Since we do not have an in-house ICP/MS system, this was our first experience working at sub ppb levels. Our first experiments with the system demonstrated that the blank levels were very high. After several changes of reagents and the installation of guard columns, the blanks were reduced drastically, but continued to be quite high, with signals corresponding to 0.2, 3 and 0.8 ppb of Pb, Zn and Cu respectively. Some detective work revealed that both the valves on our injection system, which has been in use for two years, were contaminating the system. One column of the data in Table 2, labelled "real", was collected using the less contaminated of the valves. The first set of detection limits, called "ideal", was determined using doubly distilled water in a DSI cup as the ideal blank. The improvement factors were calculated using both sets of data.

We have made no attempt in this study to demonstrate the linearity of calibration curves. Both separations methodologies [13] and DSI technologies [9] have demonstrated a linear response over at least three orders of magnitude. While this would indicate that curves would be linear, it will be critical to evaluate the performance when we move on to more extensive testing. We have also not attempted to further reduce detection limits by increasing the sample volume. Elementary theory indicates that a linear improvement would be expected as long as the column loading capacity was not approached. If implemented under the same operating conditions, the price paid would be a proportional increase in analysis time.

CONCLUSIONS

Considerable effort on our part was expended during the earlier stages of this work to develop a convenient automated FI-DSI interface. Our efforts were primarily directed at depositing the FI eluant on wire loops, which we felt would provide the best detection limits. The difficulty of achieving this interface led us to change to graphite electrodes as probes. The excellent wire loop detection limits were, in large part, due to the rapid heating of the loop. This observation encouraged us to develop an extremely thin walled, narrow stem electrode. This does not imply that graphite cups are necessarily the ultimate solution. Our expectation is that a system which sprays the eluant onto a hot surface would provide a suitable interface. The surface could be either a DSI probe or an electrothermal vaporization (ETV) system. The ETV configuration offers a number of potential advantages which are worth mentioning.

1. Convenient control of the drying step since the capability is integral in the design.
2. Rapid switching between conventional liquid introduction and ETV introduction.
3. More control of the experiment by decoupling the vaporization and excitation systems.

It is important to note that some elements generally do not provide the excellent performance of the elements selected for this test, due to the formation of non-volatile carbides. This is not to say that these elements can not be determined by this approach; there appear to be at least two ways to address the problem. The first is to use metallic DSI probes [9,11] or ETV boats. There would then be some concern that the acidic solutions used with an ion exchange preconcentration column would corrode the probe and introduce significant contamination. There are several FI preconcentration modes [8,14] which elute the analyte in a complexed form after either an ion exchange or an adsorption column. The eluants are considerably less corrosive than the strong nitric acid that is used for traditional ion exchange. Alternatively, if the complex can survive the drying process on a graphite surface, it may provide a volatile carrier for the bound metals, thereby furnishing even better performance (sharper peaks) while reducing concerns about carbide formation.

We are pleased to observe the multiplicative effect that one would expect with a complementary hybrid arrangement of this type. FI-DSI-ICP spectrometry seems to offer the potential for bringing ICP/MS detection limits to ICP-AES, as well as providing the other advantages of FI sample handling. While not demonstrated in this work, a natural by-product of the separation phenomenon would be a reduction of ICP/MS matrix effects, perhaps to levels matching or less significant than those of ICP-AES. One would also expect detection limit benefits for FI-DSI-ICP/MS to accrue.

DSI systems have demonstrated relative standard deviations of less than 1%. Similar performance is possible with FIA systems. Our precision of 4% leads us to believe that there are significant advantages to be gained in detection limits, reproducibility, and general operating performance, by developing an automated interface between the FI and the DSI systems. In fact, an automated interface would seem to us to be one of the most important obstacles to overcome before this technique can achieve a wide level of acceptance.

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G5

AUTOMATABLE TOTAL CYANIDE ANALYSIS.

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The analytical determination of the "total cyanide" concentration is very important for many industrial applications and for environmental protection, regulation and process control. Gold and silver extraction by cyanidation and froth flotation are the principal industrial applications for cyanide. According to Von Michaelis (1), about 41% of the cyanide consumed in gold and silver recovery is consumed in South Africa where about two thirds of the "free" world gold is produced, while Canada consumes about 7.1% of the world cyanide consumption. Since the simple cyanide and some of the metallocyano complexes are toxic or extremely toxic, they are subject to governmental regulations for worker safety and environmental discharge. According to the Ontario regulations, the maximum acceptable level of cyanide for drinking water is 0.2 mg/L (2). The discharge of cyanide in South Africa is regulated in terms of "total" cyanide with a maximum allowable level of 0.5 mg/L (3). The U.S. Environmental Protection Agency (EPA) water quality criterion to protect freshwater aquatic life is 3.5 μg/L of free cyanide as a 24-hour average, and the concentration should not exceed 52 μg/L at any time (4).

The term "total cyanide" is used for all cyanides, i.e. free as well as coordinated cyanide in a sample. The concentration of free cyanide in a solution depends on the pH value of the solution and on its content of heavy metals capable of forming cyanide complexes (5). Depending on their stability constants, complexed metal cyanides vary in toxicity. The ionization of such complexes, changes in pH, or photo-decomposition caused by sunlight, can result in the formation of molecular hydrogen cyanide which is a very toxic gas.

Recently, "total cyanide" determination has become the subject of numerous published papers, which include the use of a variety of methods such as titrimetry, colorimetry, cyanide-selective electrodes, coulometry, gas chromatography, high performance liquid chromatography, polarography, and atomic absorption, but still an appropriate method free from matrix interferences is not available. Liu et al (6) emphasize that the standard methods for cyanide analysis use acid distillation procedures to decompose metal cyanide complexes, but these methods have several drawbacks. The acid distillation procedure is very time-consuming and labour intensive. The methods also suffer seriously from a number of interferences such as sulphide and thiocyanate. To avoid the problems and safety handling aspects, automatable methods would be preferred. Some automated methods have been suggested by many authors, but most still are preceded by a tedious manual distillation procedure if the "total cyanide" value is desired. Zhu and Fang (7) stress that stringent control of cyanide in industrial effluents demands automation so that determinations can be repeatedly conducted preferably at intervals of a few minutes for extended periods. These authors claim that the serious potential hazard of cyanide exposure can be lowered if the distillation process is not incorporated in the system.

Liu et al (6) have suggested a different approach to cyanide detection based on the photodissociation reaction of metal cyanide complexes under UV irradiation in an acidic medium using an automated system. Many authors have shown that metal-cyano complexes can undergo photodisruption when they are exposed to ultraviolet irradiation, but stable cyano-complexes such as $Fe(CN)_6^{-4}$, $Fe(CN)_6^{-3}$ and $Co(CN)_6^{-3}$ are difficult to completely photodissociate. This cyano-ligand displacement from the coordinated cyanide does occur with UV irradiation, but UV irradiation can also result in the decomposition of thiocyanate to form sulphide and cyanide or can affect other sulphur species present in the solution. Special precautions must be taken to prevent these interferences which could produce a positive interference. Sample pretreatment is an important procedure to prevent interferences. Nonomura (8) has reported an optimized analytical procedure for the determination of total cyanide which avoids this positive thiocyanate interference.

The ultraviolet photochemical decomposition combined with the Ion Chromatography (IC) method, has been used as the basis for our research. Electrochemical detection (EC) is an appropriate way of detecting low amounts of simple/free cyanides in solution. One of the advantages of using IC with EC detection is the low amount of sample required and the rapid response obtained, as well as the sensitivity of detection. UV spectrophotometric detection was used with the IC in order to check or confirm the metal-cyano complex disappearance. In addition, a cyanide specific ion electrode was used for simple cyanide detection. In order to achieve an optimal photodecomposition, the research is focused on the analysis of the specific wavelength photosensitivity of the cyanide complexes and optimized reducing conditions.

EXPERIMENTAL SECTION

REAGENTS. Standard Cyanide Solution. 1000 mg CN^-/L of NaCN in 0.01M NaOH, prepared from analytical grade reagents and deionized water. Working solutions were prepared by dilution. Standardization was carried out using $AgNO_3$.

Standard Ferrocyanide Solution. 100 mg CN^-/L of $K_4[Fe(CN)_6].3H_2O$ (99% purity) in 0.01M NaOH for IC method and 0.1M NaOH for the specific ion electrode method for ionic strength adjustment, prepared from analytical grade regents and deionized water. Working solutions were prepared by dilution.

Standard Ferricyanide Solution. 100 mg CN^-/L of $K_3[Fe(CN)_6]$ (99.92% purity) in 0.1M NaOH for the specific ion electrode method for ionic strength adjustment, prepared from analytical grade reagents and deionized water. Working solutions were prepared by dilution.

ELUENTS.
Eluent 1. 0.01M NaOH prepared from analytical grade reagent and deionized water.

Eluent 2. 20 mM NaOH, 15 mM NaCN and 30 mM $NaClO_4$.(9).

EQUIPMENT. A Dionex 2000 Ion Chromatography was used, having an AS5 separating column and an electrochemical cell or a UV spectrophotometer after the column. A loop sample size of 10 µL was used in the injection valve and an eluent flow of 2 ml/min was set.

A Dionex potentiostat was set-up with an applied potential 0.15 V vs. Ag/AgCl and the output was sent to a recorder for peak height measurement.

A Waters Millipore spectrophotometer, model 481, was used at 0.05 AUFS with a specific wavelength for each metal cyano complex.

An Orion cyanide electrode, model 94-06 was used with an Orion specific ion meter, model 720A.

An Oriel 500 Watt mercury lamp, model 6285, was operated at 74 volts and 5.3 amperes as the UV irradiation source.

GENERAL PROCEDURE. 10 ml of fresh solutions of ferri or ferrocyanide prepared by dilution from the stock solution, having either 7 mg CN^-/L for IC measurements or 10 mg CN^-/L for the specific ion electrode measurements, were irradiated with UV for a period ranging from 1 to 15 minutes. The free cyanide produced by photolysis was detected in the solution using both methods (specific ion electrode detection and IC using both EC and UV detection). With the IC method using EC detection, eluent 1 was used. The remaining metal-cyano complex, was checked using IC with UV detection, and eluent 2 was used. For the specific ion electrode measurements ionic strength adjustment was achieved by diluting the ferri or ferrocyanide stock solution with 0.1 M NaOH to 10 mg CN^-/L.

For the effect of temperature on ferrocyanide solutions, 10 ml of fresh solutions of ferrocyanide prepared from the stock solution, having 7 mg CN^-/L, were held in a bath at 5°C or 45°C and were UV irradiated.

RESULTS AND DISCUSSIONS.

CALIBRATION CURVES. The standard calibration curve for cyanide measurement using the specific ion electrode shown in Figure 1(a), illustrates linearity between millivolts and concentration of the cyanide solution from 0.5 to 20 mg CN^-/L. Data follows the regression curve: log(conc.) = 0.016818*mV - 2.003036, where concentration is given in mg CN^-/L. The correlation coefficient is 0.9978 and concentrations were determined with in ± 3.7%. A typical calibration curve for cyanide measurement using IC with EC detection is shown in Figure 1(b), having a correlation coefficient of 0.999 and concentrations were determined with in ± 0.5%. For the measurement of the unknown solutions of photodissociated cyanide using IC with the EC detection, a calibration curve was prepared immediately before the measurements because of day to day variability in the calibration curve. No linear region was found for these calibrations.

The standard calibration curve for ferrocyanide measurements using UV spectrophotometric detection is shown in Figure 2(a), and it shows linearity between peak size (mm) and cyanide concentration (mg/L). Data follows the regression curve: CN^- conc.(mg/L) = (peak - 0.411966)/7.244083, where peak size is given in millimetres. The correlation coefficient is 0.9983 and concentrations were determined with in ± 4%.

UV IRRADIATION OF SODIUM CYANIDE. When the sodium cyanide solution was U.V. irradiated, a constant value of cyanide was obtained using both methods for the detection of cyanide as shown in Figure 2(b). The CN^- concentration of the solution for specific ion electrode was 10 mg/L and for the IC with EC detection 7 mg/L. This shows UV irradiation that the simple cyanide was not photosensitive to UV irradiation under the test conditions and that both detection methods were suitable for free cyanide determination.

UV IRRADIATION OF FERROCYANIDE SOLUTION. Solutions of potassium ferrocyanide with pH about 12 were UV irradiated for various times and the amounts of free cyanide produced were measured by both IC with EC and the specific ion electrode. The results are presented in Figure 3 as percentage free cyanide recovered. In our experiments, 98% of CN^- recovery was measured after 5 minutes of UV irradiation, with the use of the specific ion electrode method; and 100% recovery with the use of the IC method with the EC detection. The disappearance of ferrocyanide was followed with the IC using UV spectrophotometric detection set at 220 nm, and complete disappearance of ferrocyanide was found after 10 minutes of radiation (see Figure 3). A gradual photodissociation of the metal complex was observed with time. According to many authors, ferrocyanide changes rapidly to the $(Fe(CN)_5H_2O)^{-3}$ with the liberation of the cyanide ligand, however in our work complete photodissociation was found after 10 minutes showing a complete disappearance of $(Fe(CN)_5H_2O)^{-3}$. Otake et al.(10), claim that the rate of disappearance of ferrocyanide and $(Fe(CN)_5H_2O)^{-3}$ were zero order with respect to the concentration of the species and both rates were independent of reaction temperature, but varied with the pH value and the light quanta absorbed by the solution. The use of the UV spectrophotometer confirmed the fact that ferrocyanide dissociated. This ferrocyanide dissociation can be accelerated if the UV intensity is increased by increasing the applied voltage to the Hg lamp.

EFFECT OF TEMPERATURE ON UV IRRADIATION OF FERROCYANIDE. The time of radiation causes a temperature rise in the ferrocyanide solution. This gradual increase in temperature with time is shown in Figure 4. This variation in the temperature is important because the rate of ferrocyanide photodissociation may be temperature dependent. For this reason, the rate of ferrocyanide photodissociation was studied at different temperatures. Contrary to Otake et Al's work, the rate of photodissociation for the ferrocyanide solutions increased with the temperature of the solution as shown in Figure 5. For the solution held at a temperature of 5°C, 90% of ferrocyanide dissociation was achieved at 10 minutes. For the solution held at 45°C, that photodissociation was achieved at 4 minutes (see Figure 5). Thus, elevated temperatures could be used to reduce irradiation time.

U.V.IRRADIATION OF FERRICYANIDE SOLUTION. A solution of potassium ferricyanide with a pH about 12 was UV irradiated and the free cyanide produced was detected with the specific ion electrode method. A maximum of about 80% of cyanide recovery was obtained after 7 minutes and decreased to 72% after 15 minutes. Since the recovery of ferricyanide was only 80% but the recovery of ferrocyanide was quantitative, the use of a reducing agent was indicated. Various reducing agent were tested (sodium borohydride, 0 to 250 mg/L of ferricyanide solution; 50% v/v hypophosphorous acid, 0% to 10% v/v in the ferricyanide solution; and hydrazine, 0.1 to 100 mg/L of ferricyanide solution). The highest recovery was found with 0.5% of 50% v/v hypophosphorous acid. The results with this reducing agent are shown in Figure 6. After 10 minutes of UV irradiation, 98% cyanide recovery was achieved.

CONCLUSIONS.

The following conclusions are based on the initial results of this study.

(1) The specific ion electrode had a linear response over cyanide concentrations from 0.5 to 20 mg/L. Concentrations were determined with in ± 3.7%.

(2) IC with EC detection did not show a linear response even over a relative narrow CN^- concentration range 0 to 7 mg/L. A smaller size of the micro-loop may be needed to obtain linearity. A calibration curve must be performed with the measurements since the calibration varies from day to day. Concentrations were determined with in ± 0.5% in most of the calibrations.

(3) IC with UV spectrophotometric detection had a linear ferrocyanide response over the range 0 to 7 mg CN^-/L. Concentrations were determined with in ± 4.0%.

(4) No UV photodecomposition of simple CN^- was observed when sodium cyanide solutions were UV irradiated.

(5) Quantitative yield of cyanide recovery was found for ferrocyanide solutions after 10 minutes of UV irradiation.

(6) Temperature could be used to increase rate of cyanide recovery from ferrocyanide solutions.

(7) Quantitative yield (98%) of cyanide recovery from ferricyanide solutions required a reducing agent. The best reducing agent tested was 0.5% of 50% v/v hypophosphorous acid.

FUTURE WORK.

This project will a) demonstrate that quantitative decomposition of other metal cyanide complexes can be accomplished without causing cyanide loss, b) that the thiocyanate ion is not decomposed under the required radiation conditions, c) that there are no other interferences that bias the total cyanide values, and d) describe an appropriate automatable system.

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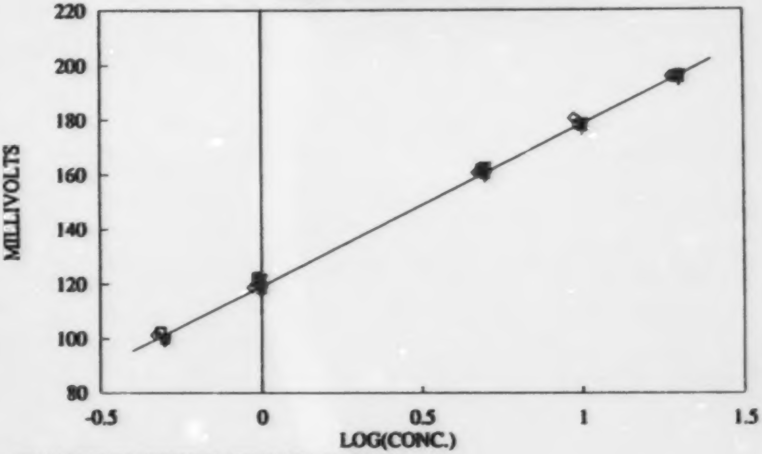
FIGURE 1(a): CYANIDE CALIBRATION
USING SPECIFIC ION ELECTRODE



CYANIDE CONCENTRATION IS GIVEN IN mg/L.

FIGURE 1(b): CYANIDE CALIBRATION
USING ELECTROCHEMICAL CELL

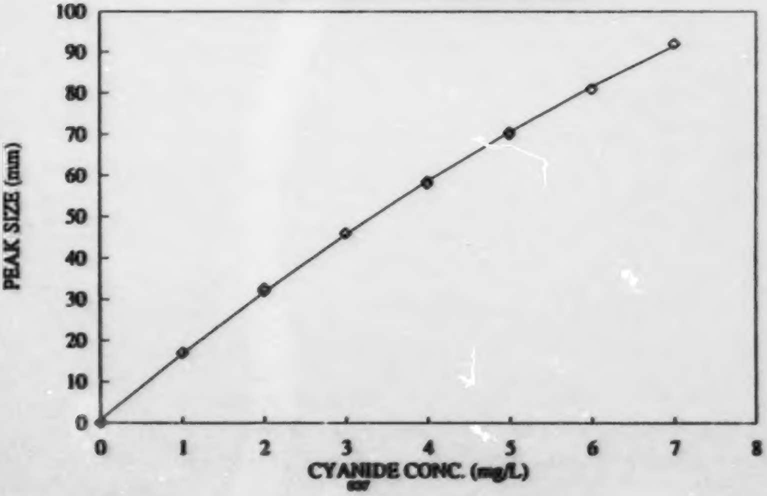


FIGURE 2(a): FERROCYANIDE CALIBRATION
USING UV SPECTROPHOTOMETRIC DETECTOR

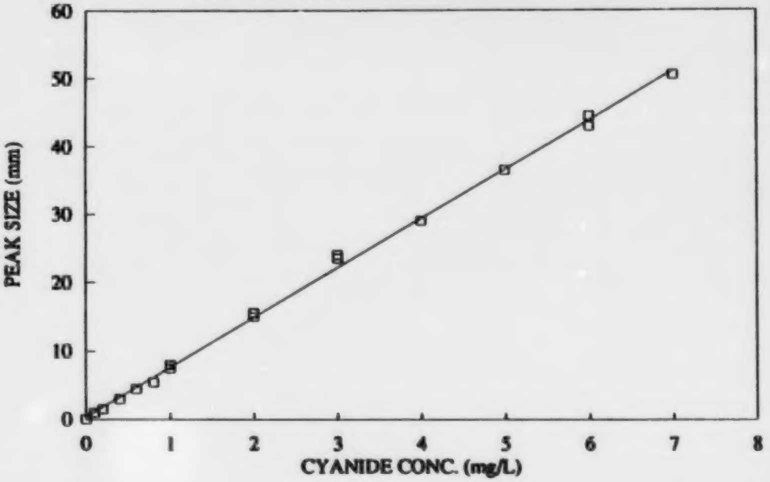


FIGURE 2(b): CYANIDE UV IRRADIATION
USING SPEC. ION ELECTRODE AND EC CELL

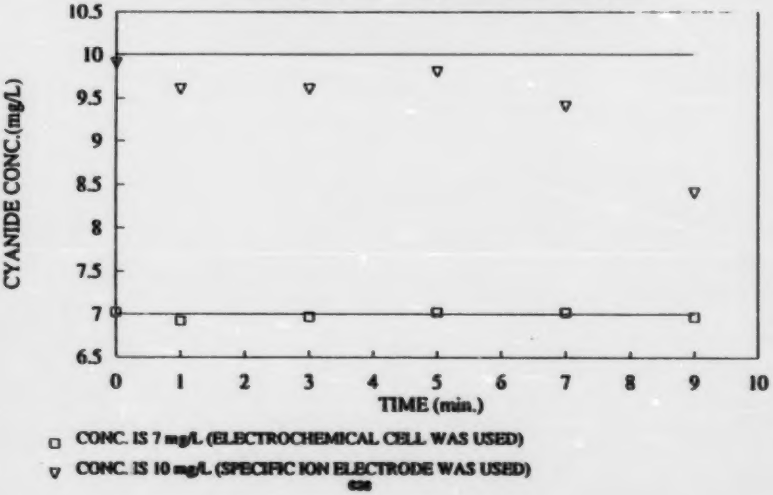


FIGURE 3: FERROCYANIDE UV IRRADIATION

DISSOC. AND NON-DISSOCIATED CYANIDE AFTER UV IRRADIATION

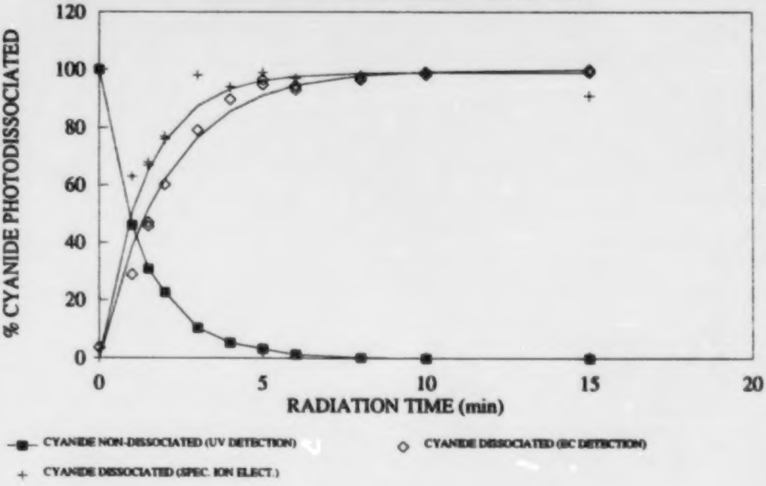


FIGURE 4: TEMPERATURE-IRRADIATION TIME

FERROCYANIDE SOLUTION

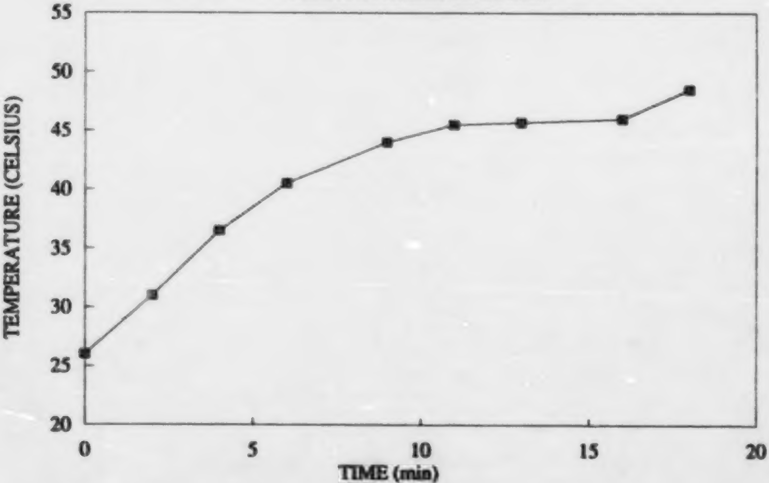


FIGURE 5: FERROCYANIDE PHOTODISSOCIATION

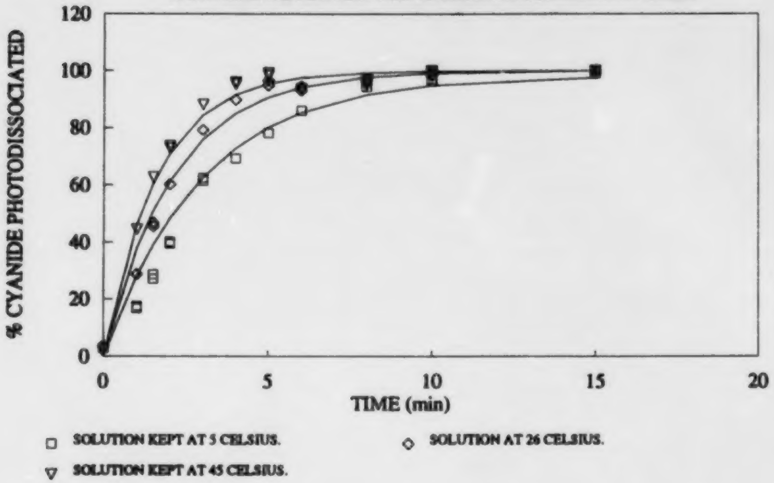
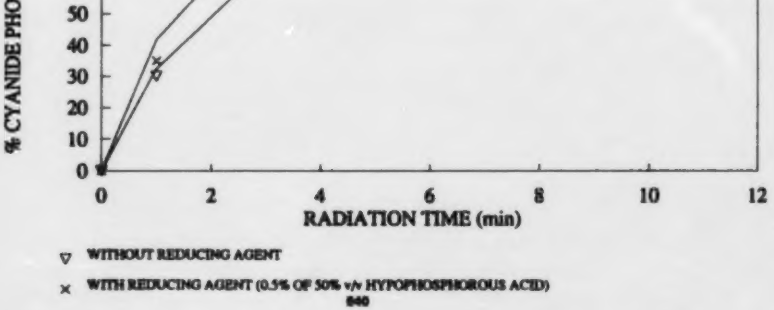


FIGURE 6: FERRICYANIDE PHOTODISSOCIATION



G6

THE USE OF ENVIRONMENTAL ISOTOPE SURVEYS IN ASSESSING CONTAMINATION POTENTIAL OF "CONFINED" AQUIFERS

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ABSTRACT

The "freshwater aquifer" is a widely-used, regional aquifer which underlies most of Essex, Kent, and Lambton Counties in southwestern Ontario. It consists of fractured bedrock subcrop plus a thin layer of overlying granular material. Even though the aquifer in the central part of Essex County is remote from the obvious recharge area and is covered by more than 25 m of clayey overburden, it contains groundwater that appears to be less than about 40 years old (Crnokrak, 1991). This enclave of anomalously young groundwater coincides with a linear morphological feature mapped by Morris (pers. comm.). We used a program of exploratory drilling, hydrometric monitoring, environmental isotope tracing, and natural geochemical tracing to determine if the feature can explain the rapid recharge of the freshwater aquifer. This paper outlines the problem and briefly summarizes our initial results.

INTRODUCTION

Objectives

The main goal of this study is to determine whether a linear morphological feature, reported to be an esker buried beneath clayey overburden, is responsible for the anomalously young groundwater noted in the central part of the freshwater aquifer in Essex County, Ontario. The primary objectives in the first year of the study were to: (1) verify the existence of the buried esker reported by Morris (pers. comm.), (2) verify the existence of the anomalously young groundwater in the freshwater aquifer, and to (3) examine the spatial relationship between the young groundwater and the feature.

The Problem

The "freshwater aquifer" is a widely-used, regional aquifer which underlies most of Essex, Kent, and Lambton Counties in southwestern Ontario. Regionally, the aquifer consists of fractured bedrock subcrop and generally not more than a few metres of granular material. The aquifer thickens considerably in bedrock valleys such as the one in Sarnia (Intera Technologies Ltd., 1987). Dillon (1987) estimate that the horizontal groundwater velocity in the freshwater aquifer in central Essex County is in the order of 2.5 m/a.

The clayey overburden overlying the freshwater aquifer commonly exceeds 30 m. According to Desaulniers et al. (1981), this overburden is usually thick enough and of sufficiently low permeability (in the order of 2 x 10^{-10} m/s) to be widely suitable for waste disposal. Ruland et al. (1991) conclude that active groundwater flow in the clayey overburden is restricted to the upper several metres. Recent research by D'Astous et al. (1989), however, raises some doubt about our ability to accurately characterize the hydraulic conductivity of the fractured clays that commonly occur throughout the region.

At the University of Windsor, we have mapped the distribution of environmental isotopes (oxygen-18 and tritium) in the freshwater aquifer in Essex, Kent, and Lambton Counties. The distributions of theses isotopes reflect the natural recharge, discharge, and flow directions in the aquifer. The distinctive input functions of these isotopes can be used to differentiate between groundwater recharged thousands of years ago and groundwater recharged within the last few decades. Fritz and Fontes (1980) and others give details about the use of oxygen-18 (^{18}O) and tritium (^{3}H) in hydrogeologic studies.

Figure 1 from Crnokrak (1991) shows the distribution of ^{18}O in the freshwater aquifer in Essex County. ^{18}O analyses are expressed in the standard del (δ) notation in parts per mil (o/oo) difference relative to the international standard SMOW (Standard Mean Ocean Water)(Craig, 1961), where: $\delta^{18}O = [(R_x - R_{SMOW})/(R_{SMOW})] \times 1000$; where: $R = {}^{18}O/{}^{16}O$ and x = sample. The analytical precision for ^{18}O measurements by mass spectrometry is better than ± 0.2 o/oo.

Figure 1 is based on groundwater collected from 35 domestic wells completed in the freshwater aquifer. According to Crnokrak (1991), Desaulniers et al. (1981), and Edwards and Fritz (1988), the $\delta^{18}O$ values in the northeast and northwest parts of the county (-15 and -16 o/oo) indicate groundwater that was recharged during cooler climatic conditions more than 10,000 years ago. The relatively enriched $\delta^{18}O$ values found in the groundwater in the southern and central parts of the county (-8 to -10 o/oo) are indicative of groundwater recharged under the milder climatic conditions of the past 10,000 years.

Crnokrak (1991) reports that the electrical conductivity (EC) and ^{3}H distributions are consistent with the ^{18}O distribution. She observed EC values in the freshwater aquifer greater than 3000 μS/cm in the northeast and northwest parts of the county, while the EC values are less than 500 μS/cm where the relatively enriched $\delta^{18}O$ values occur.

More significantly, the groundwater in the enclave of enriched $\delta^{18}O$ values in central Essex County have ^{3}H concentrations characteristic of recharge since 1952. Groundwaters recharged since 1952 contain anthropogenic ^{3}H derived from atmospheric testing of nuclear bombs. These groundwaters are characterized by ^{3}H concentrations exceeding 3 TU, where: 1 TU = 1 tritium unit = $1\,^{3}H$ in 10^{18} ^{1}H atoms. Groundwaters recharged prior to 1952 contain only cosmogenic ^{3}H that has now been reduced by radioactive decay to concentrations less than 3 TU.

The location of this enclave of young groundwater is puzzling. Rapid vertical recharge through the thick aquitard has been considered to be unlikely in view of the isotopic studies

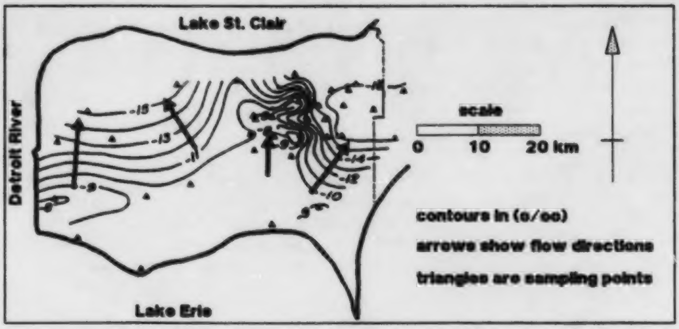

Figure 1. Distribution of oxygen-18 in the freshwater aquifer (after Crnokrak, 1991).

by Desaulniers et al. (1981). Lateral flow from the closest obvious recharge area also seems improbable given the low groundwater velocity in the aquifer reported by Dillon (1987).

Although Crnokrak's (1991) ^{18}O distribution map for the freshwater aquifer may be explained using the groundwater velocity reported by Dillon (1987), her ^{3}H distribution map cannot be explained in this manner. Groundwater containing anthropogenic ^{3}H should only be found within a few hundred of metres of the recharge area. The nearest surface expression of the aquifer recharge area, however, is more than 10 km upgradient from some of the tritiated groundwater in the freshwater aquifer reported by Crnokrak (1991).

A clue to the origin of this young water may lie in the study by Morris (pers. comm.). Based on remote sensing, field mapping, and drilling data, Morris (1989) mapped a linear morphological feature in central Essex County that he concludes is a buried esker. Morris (1989) first noted the feature by lighter tones on remote sensing images. There are no other obvious surface expressions of this feature. While comparing data in the summer of 1989, we noted that Morris' linear morphological feature coincided with Crnokrak's enclave of anomalously young groundwater in the freshwater aquifer.

We began with two hypotheses to explain the young groundwater. First, groundwater velocities are very high along the reported esker enabling rapid lateral groundwater movement from the closest obvious recharge area. Second, precipitation has recharged the freshwater aquifer rapidly by infiltrating through localized deep vertical fractures through the aquitard which are related to the settlement of the clayey deposits over the buried esker.

METHODS

Our general approach to the problem has been to assess groundwater ages and flow directions along, and perpendicular to, the linear morphological feature. To do this, we examined ^{18}O, ^{3}H, EC, and hydraulic head distributions in the vicinity of the feature. We installed monitoring wells in two transects across the feature (Sites 1 and 2 on Figure 2) and extended the network with nearby domestic wells. Figure 2 also plots the trace of the linear morphological feature reported by Morris (pers. comm.).

At both Sites 1 and 2, we attempted to drill a "deep" hole through the crest of the feature and on to bedrock to determine the stratigraphy and the depth to the top of the aquifer. Since the feature has no surface expression, this proved difficult. After installing a monitoring well in the deep hole, we completed the transect with a two or three level piezometer nest and one or two additional wells screened in the aquifer within a distance of about 200 m.

We squeezed porewater from Shelby tube samples of clayey overburden that were taken every 3 m from one deep hole at each site. These samples were used to determine the vertical distribution of ^{18}O. Samples from the monitoring and domestic wells were analyzed for ^{18}O, ^{3}H, and EC.

Samples for ^{18}O analysis were prepared at the University of Windsor and analyzed at the University of Ottawa. Samples for ^{3}H analysis were run at the Isotope Laboratory, Department of Earth Sciences, University of Waterloo. Samples from Sites 1 and 2 were analyzed for ^{3}H using the enriched technique which has a precision of better than 1 TU. Samples from the domestic wells were analyzed using the direct method which has a precision of about ± 8 TU. According to Egboka et al. (1983), ^{3}H values of less than 15 TU by the direct method almost always mean that less than 1-2 TU are actually present.

RESULTS AND DISCUSSION

We drilled 9 boreholes in the two transects. Figure 3 shows the geologic cross-section for Site 2. All of the drill sites are dominated by clayey silt to silty clay grey till interbedded with numerous sand units. Bedrock was encountered at between 31 and 34 m below ground surface. At Site 2, we encountered almost 5 m of coarse granular material above bedrock at AMA-90-4a. At wells AMA-90-5 and 6, located 31 and 68 m north of AMA-90-4a, the thick layer of coarse granular material was not encountered. We did not encounter a similar coarse granular unit at Site 1.

Although the regional map of hydraulic head in the freshwater aquifer suggests that groundwater flows from the feature outward (Crnokrak, 1991), the hydraulic head data from Sites 1 and 2 give no clear indication whether the feature is a recharge area.

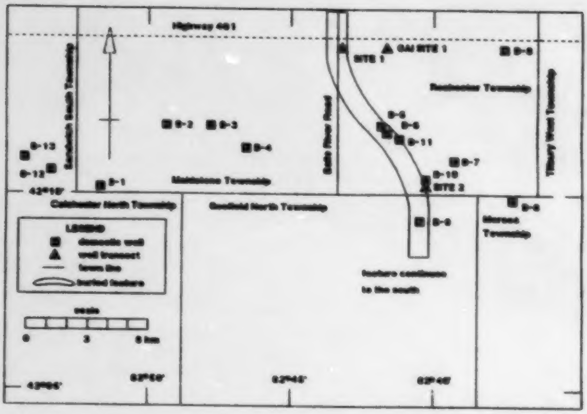
Highway 401
SITE 1
SITE 1
D-1
D-2
D-3
D-4
D-7
D-10
SITE 2
D-11
D-12
D-13
Sandwich South Township
Maidstone Township
Rochester Township
Tilbury West Township
Colchester North Township
Gosfield North Township
Mersea Township
LEGEND
domestic well
well transect
town line
buried feature
feature continues to the south
scale
0
3
6 km
42°10'
42°04'

Figure 2. Locations of monitoring and domestic wells.

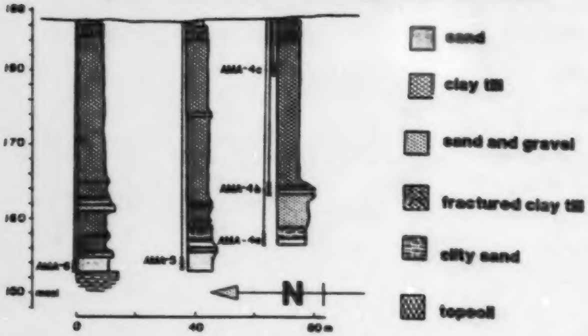
180
170
160
150 masl
AMA-4c
AMA-4b
AMA-4a
AMA-5
AMA-6
N
0
40
80 m
sand
clay till
sand and gravel
fractured clay till
silty sand
topsoil

Figure 3. Geologic cross-section at Site 2.

The direction of the hydraulic gradient along the feature, from south to north, is consistent with the regional trend. From Site 2 to Site 1, the hydraulic gradient is approximately 0.0004. This is somewhat lower than regional lateral hydraulic gradients noted by Dillon (1987).

Assuming the highest observed hydraulic conductivity value (1.3×10^{-3} cm/s) and a porosity of 0.3, the groundwater velocity along the feature from Site 2 to Site 1 would be about 1.3 m/a. Although this velocity is consistent with the Dillon (1987) value, it cannot explain the presence of post-1952 water in central Essex County by lateral flow. Even if we have underestimated the velocity by a factor of 10, we could still not explain post-1952 water in central Essex County.

The vertical hydraulic gradient at Site 1 is upward (0.063), as expected, since the wells in the aquifer are flowing. This suggests discharge rather than recharge. At Site 2, the hydraulic gradient is downwards (0.003) suggesting recharge.

The preliminary isotopic and EC data (Table 1) are consistent with young groundwater in the freshwater aquifer around the feature. The more enriched $\delta^{18}O$ values that reflect more recnt recharge are found near the feature. The ^3H data indicate that groundwater recharged since 1952 exists at Site 2 and at domestic wells on and near the feature. Elsewhere, the tritium data indicate pre-1952 recharge. The EC values suggest fresher water near the feature.

Studies by Desaulniers et al. (1981) and Sklash and Ibrahim (1991) have reported progressively more depleted $\delta^{18}O$ values with depth in porewater in the clayey overburden in Essex County (Figure 4). These studies conclude that the groundwater in the lower parts of the clayey aquitard were recharged under cooler climatic conditions and are several thousand years old. The $\delta^{18}O$ values in this study are almost constant with depth. The very depleted $\delta^{18}O$ values noted by others at the base of the aquitard are absent.

Our results imply much younger water in the clayey aquitard and much more rapid vertical movement of groundwater through the aquitard than reported in previous studies. The $\delta^{18}O$ distribution in the clayey overburden also suggests that the young groundwater in the aquifer is the result of vertical recharge rather than lateral arrival via the feature. The difference between the $\delta^{18}O$ distributions at Sites 1 and 2 may reflect the differences in vertical hydraulic gradient direction at the sites.

CONCLUSIONS

We used a program of drilling, hydrometric monitoring, and environmental isotope and natural chemical tracing to determine: (1) if the linear morphological feature noted by Morris (pers. comm.) in central Essex County is a buried esker, (2) if the groundwater in the freshwater aquifer around the feature is anomalously young as noted by Crnokrak (1991), and (3) to examine the spatial relationship between the young groundwater and the feature. The drilling results at Site 2 are not inconsistent with the linear morphological feature being a buried esker. The groundwater in the freshwater aquifer around the feature at Site 2 has apparently recharged within the last 40 years. Although relatively young groundwater resides near Site 1, the water is older than 40 years old. Our findings at Site 1 suggest that either the feature is much more subdued there or that we missed the feature.

Table 1. Selected chemical and isotopic data.

WELL #	DEPTH (m)	EC (µS/cm)	$\delta^{18}O$ (o/oo)	T (TU)
SITE 1				
Well 1	31.70	1650	-12.2	<0.8
Well 2a	27.80	1793	-11.0	<0.8
Well 2b	7.62	2221	-12.2	<0.8
Well 3	31.09	1432	-11.9	<0.8
SITE 2				
Well 4a	30.48	343	-10.0	<0.8
Well 4b	23.16	318	-7.5	2.6
Well 4c	7.62	563	-9.2	2.3
Well 5	33.68	294	-9.6	<0.8
Well 6	34.14	371	-8.8	5.0

WELL #	EC (µS/cm)	$\delta^{18}O$ (o/oo)	T (TU)
DOMESTIC WELLS			
B-1	718	-13.3	<6
B-2	605	-14.3	10
B-3	1026	-10.7	16
B-4	2200	-16.1	<6
B-5	796	-8.3	15
B-6	476	-8.0	21
B-7	465	-9.7	<6
B-8	1530	-11.1	<6
B-9	470	-9.7	<6
B-10	354	-9.4	14
B-11	448	-9.6	<6
B-12	1502	-13.0	<6
B-13		-9.6	<6

Site 1 and 2 well tritium analyses ± 0.6 TU
Domestic well tritium analyses ± 8 TU

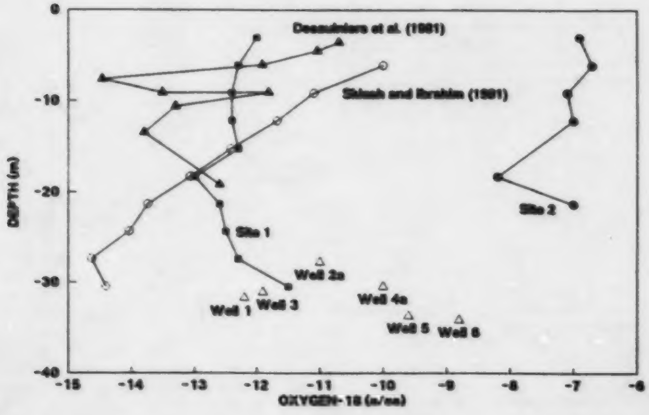

Figure 4. Vertical distribution of oxygen-18 in the clayey overburden.

The ^{18}O distributions with depth at both sites suggests more rapid vertical infiltration than at other sites studied in Essex County. These results also suggest that vertical infiltration, rather than lateral inflow, is responsible for the young groundwater in the freshwater aquifer.

We are currently trying to obtain a better spatial definition of both the feature and the young groundwater by adding to our existing transects and by adding new transects to our monitoring network. In addition, we are examining the fracture distributions and orientations in transects across the feature.

ACKNOWLEDGEMENTS

We thank Blagy Novakovic of the Ontario Ministry of the Environment and Tom Morris of the Ontario Geological Survey for their useful suggestions. The Ontario Ministry of Transport and the Township of Rochester permitted us to drill on their right-of-ways. Ontario Ministry of the Environment Research Grant Project No. 500G made this project possible. Funding from the Ontario Ministry of the Environment Environmental Youth Corps and Employment Canada SEED programs allowed us to hire additional field assistants.

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GENETICALLY ENGINEERED RESISTANCE TO POTATO VIRUS X IN FOUR COMMERICAL POTATO CULTIVARS

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ABSTRACT

The coat protein gene from potato virus X (PVX) was introduced into four potato cultivars using a disarmed binary vector and Agrobacterium tumefaciens transformation system. Transgenic potato cultivars were shown to express the viral capsid protein and were resistant to PVX infection. The coat protein mediated protection resulted in a drastic reduction of the virus accumulation in transgenic potato cultivars in comparison to non-transfromed cultures.

INTRODUCTION

Potato virus X (PVX) is the most widespread of potato viruses and often completely infects certain commercial stocks with yield reductions estimated up to more than 15%. PVX may be latent, without foliage symptoms or apparent effect on plant vigor except when closely compared to PVX-free stocks. Dual infections of PVX and potato virus Y (PVY) may show a synergistic increase in disease symptoms and severity known as "rugose mosaic"[1]. PVX infection is systemic in the Solanaceae, usually produces local lesions in the Chenopodiaceae or Amaranthaceae and also infects certain Leguminosea. PVX is, with few exceptions, transmitted vegetatively by tubers in susceptible cultivars. Transmission through sap inoculation is accomplished by contact of plant parts in the field due to wind, animals or machinery.

PVX has many strains and the relationship among these strains has also been reported. These strains can be classified into four groups on the basis of serology and infectivity for different potato varieties[2]. In plant cross-protection tests, strains of PVX may protect against the effects of one another completely, partially or not at all. The term of cross-protection is specifically applied to the protection of a plant by a mild strain of a virus or from subsequent infection by a virulent strain of the same virus[3]. The application of cross-protection in controlling plant virus diseases has been practised in some countries and has met with some successes. However, classical cross-protection is not recommended as a general practice because the so-called mild strains often reduce yield by about 5-15%, there are no appropriate mild strains of some viruses available and the practice for field use is laborious. The dominant strain of a virus may change to a non-virulent strain, and the dangers of double infections and spreading to other crops still exists[4]. However, cross-protection induced by genetic engineering overcomes these problems. Introduction and expression of foreign genes in plants with the disarmed Ti plasmid of Agrobacterium tumefaciens using a binary system[5] is well documentated. Tobacco plants genetically engineered to express the coat protein genes of TMV[6-9], Cucumber Mosaic Virus (CMV)[10], PVX[11] Alfalfa Mosaic Virus (AlMV)[12,13] and Tobacco Rattle Virus (TRV) can be protected against subsequent infection of these viruses.

Potato plants genetically engineered to express the coat protein genes of PVX[15] and PVX and PVY[16] can also be protected against subsequent infections of these viruses. The mechanisms of protection may be similar to that of classical cross protection where the uncoating of the virus is inhibited and early events in RNA replication are moderated. The plant encoded coat protein might prevent virus disassembly, recoat the RNA as it is stripped, interfere with the putative receptor site on the host, or act by some other as yet unidentified mechanisms[17].

In this study the coat protein gene (CP) of PVX was cloned between the 35S promoter of cauliflower mosaic virus (CaMV)) and the nopaline synthase (NOS) transcription terminator. The CP gene was then placed into a binary vector and used to transform four potato cultivars, Russet Burbank, Desirée, Shepody and Bintji. The resulting transgenic potato plants were analyzed for the expression of viral coat protein and for their resistance to PVX infection.

MATERIALS AND METHODS

Construction of recombinant plasmid of Polylink I with sub-cloned PVX cDNA 117A

PVX cDNA clone 117A representing the 3' end of the RNA was used in this study. This cDNA clone containing the capsid protein gene was first linearized with SalI, the ends were rendered blunt by filling with

Klenow fragment of *E. coli* DNA polymerase I, and then digested with XbaI. A DNA fragment of about 1.3 kbp containing the 8K protein, the coat protein and the non-coding region was isolated. DNA fragments were then purified by 1% agarose gel electrophoresis followed by electroelution. Plasmid Polyrok I was linearized with SmaI, and then digested by XbaI. The linearized plasmid and the cDNA 117A fragment were ligated with T_4 DNA ligase (Pharmacia) and transformed into *E. coli* JM101 or HB101. Bacteria harbouring the recombinant plasmid were plated onto LB plates containing kanamycin (50 μg/ml). Polyrok I is a derivative of pBin 19[9] which utilizes the trans-acting function of the vir region of the co-resident Ti plasmid in LBA 4404 to transfer sequences bordered by left and right T-DNA into nuclear genome of plants. The T region in Polyrok I contains the neomycin phosphotransferase gene (NPT II) which is driven by the nopaline synthase (NOS) promoter. The plasmid Polyrok I also contains an XbaI Sst I fragment (multiple cloning site) from pUC 19 bordered by the cauliflower mosaic virus (CaMV) promoter and a nos polyadenylation site (terminator).

Conjugation of *Agrobacterium tumefaciens* (LBA 4404 with disarmed Ti plasmid) and *E. coli* was performed in a tri-parental mating process. The donor strain *E. coli* HB 101 harbouring the recombinant plasmid Polyrok I containing the PVX coat protein gene and the helper strain, *E. coli* DH5 α containing pBRK 4013 were used in the triple mating process. Cointegrates were selected on LB plates containing kanamycin (150 μg/ml), nalidixic acid (150 μg/ml) and streptomycin (375 μg/ml).

Plant regeneration/transformation

(a) Transformation/Regeneration from tuber

Virus-free potato tubers of the following cultivars, Desiree, Russett Burbank, Shepody and Bintji were stored in the dark at 4°C. Potato tubers were washed, peeled and surface sterilized for 20 min in 1% hypochloride solution. Tubers were then washed thoroughly in large volumes of sterile water. Discs 1-2 mm thick were sliced from cylinders of tuber tissue prepared with a cork borer.

Agrobacterium tumefaciens (LBA 4404) containing Polyrok I with PVX coat-protein was grown on selective plates. Single colonies were grown overnight in liquid LB media with 100 μg/ml kanamycin. The final bacterial concentration used was 10^9 cells/ml. Approximately 5 μl of bacteria were applied to the surface of potato discs. On the surface of filter paper laid on MSI containing MS salts[9] and vitamins with 1.5% sucrose and 0.9% bactoagar. After 48 hours of co-culture, potato discs were transferred onto selection media MS 31 containing MS salts, B5 vitamins, 3% sucrose, 1 mg/l kinetin, 1 mg/l zeatin, 1 mg/l BAP, 0.5 mg/l NAA, 100 mg/l kanamycin and 400 mg/l carbenicillin, solidified with 0.9% agar. Primary shoots that develop after 3-4 weeks were cut off and remaining discs were cultured again in the same media. Secondary shoots obtained after 2-3 subcultures were transferred to MS8 medium containing MS salts B5 vitamins, 3% sucrose, 0.5 mg/l gibberellic acid, 0.5 mg/l kinetin, 100 mg/l kanamycin, 400 mg/l carbenicillin and 0.9% agar. Rooted plantes were transferred to soil and kept under polyethylene bags and high humidity for about two weeks before transferring to greenhouse conditions.

(b) Transformation/Regeneration from stem

Axenic cultures of potato cultivars were propagated *in vitro* through shoot tip cuttings and maintained in MS 8. Internodal stem explants were cut 0.5 cm in length and then cut longitudinally and then transferred to bacterial suspension for 2 min., blotted on the surface of sterile filter paper and transferred to petri dishes containing MS 1. Explants (10 per plate) were co-cultivated with *Agrobacterium* for 48 hrs., the explants were then washed in MS medium containing 1 g/L carbenicillin for 24 hrs, before being blotted dry and cultured in MS 7 medium containing B5 vitamins, 1% sucrose, 1% glucose, 1% mannitol, 1 mg/l BAP, 0.5 mg/L zeatin, 0.5 mg/l NAA, 400 mg/l carbenicillin, 100 mg/l kanamycin, solidified with 0.9% bactoagar. $AgNO_3$ 10 mg/l was included in MS 7 media with Russett Burbank tissue culture[19]. Regenerated shoots were rooted and transferred to soil as described above. All potato cultures were grown in a culture room with 22°C day, 15° night and 16 hr photoperiod with $43\mu Em^{1}$ sec^{1} light intensity.

Western blot analysis of coat protein expression

Total soluble proteins were isolated from young leaves of kanamycin resistant potato, and from healthy control plants. Leaf tissue 0.1 mg was extracted on ice with 3 ml of extraction buffer containing 0.3 M Tris-HCl, pH 8.3, 15 mM DTT, 1 mM EDTA, 1 mM phenyl methyl sulfonyl fluoride (PMSF), 1 mM Benzidin. Protein pellets were dissolved with sample buffer 0.5 M Tris-HCl, pH 6.8, 10% Glycerol, 10% SDS w/v, 5% 2-β-mercaptoethanol and 0.05% bromophenol blue and boiled at 100°C for 3 min before loading on the gel. Protein samples were run (~15 μg protein per lane) on SDS-PAGE continuous gel (12% acrylamide for separating and 4% for stacking), cross linker 0.05% for separating and 0.1% for stacking gels in the buffer system of Laemmli[29], using a Bio-Rad protein II apparatus. After electrophoresis, the gel was incubated in transfer buffer (25 mM Tris HCl, pH 8.3, 192 mM glycin and 20% methanol). Polypeptides were then transferred to nitrocellulose membranes at a constant voltage of 30 V overnight. The membranes were then washed with TBS buffer (10 mM Tris HCl, pH 8 and 150 mM NaCl), and coated with 5% skimmed milk powder. Membranes were then incubated overnight with rabbit anti-PVX coat protein polyclonal antibody conjugated to alkaline phosphatase (1:1000), then carefully washed with TBS, TBS + 0.05% w/v Tween-20 and TBS incubated with the secondary antibodies (alkaline phosphotase conjugated goat anti-rabbit IgG, BioRad, U.S.A.) (1:1000). Incubation with antibodies was carried out for 2 hrs at 22°C with constant shaking. Filters were washed as described above and incubated for 10 min in developing buffer (100 mM Tris HCl, pH 9.0; 100 mM NaCl and 50 mM $MgCl_2$). Substrate [35 μl nitroblue tetrazolium (NBT), and 27 μl 5-bromo-4-chloro-3-indolylphosphate (BCIP) in 10 ml of developing buffer] was added and incubated in the dark. Colour development is stopped by washing the filters with distilled water.

RESULTS

Construction and transfer of PVX capsid protein gene into *A. tumefaciens*

PVX is the type member of the potexvirus group. The 3' end region of the genome contains a non-coding sequence of 76 nucleotides, the CP gene which encodes for a protein of 237 amino acids (26K) which is translated from a subgenomic RNA in vivo[21]. A large fragment of about 1.3 kbp containing the 3' end region of PVX genome, th CP and 8K protein genes was introduced into the expression vector Polyrok I between the 35S promoter and the nos terminator (fig. 1). The chimeric plant expression vector was used to transform potato cultivars by an *Agrobacterium tumefaciens* - mediated transformation system. Using this transformation system, approximately 2% of the original explants produced transformed plants which expressed detectable levels of PVX coat protein. About 20 colonies were selected from the LB agar plates containing 50 μg/ml kanamycin. The recombinant plasmid of Polyrok I containing the 1.3 kb fragment of cDNA 117A was transformed into competent cells of *E. coli* JM 101. These colonies were labelled JP 117-1 to JP 117-20. Digestion of these colonies with XbaI and SacI indicated that JP 117-4, JP 117-9, JP 117-10 and JP 117-14 contained the 1.3 Kbp fragment of cDNA 117A. The recombinant plasmid JP 117-10 was then transformed into *E. coli* HB 101 and used for further studies. The result of Tri-parental mating of LBA 4404, *E. coli* DH 5 α and *E. coli* HB 101 (containing HP 117-10) indicated that recombinant plasmid HP 117-10 has been introduced into Agrobacteria. Similar results were obtained after transformation of the chimeric Polyrok I containing the PVX CP protein gene directly into *A. tumefaciens*.

Transformation and regeneration

Four different cultivars of potato, Desirée, Bintji, Russet Burbank and Shepody were used for transformation experiments. Both tuber and stem tissues were used for transformation. Primary shoots regenerated from potato tuber discs about one week after subculture into MS 31. Transformation efficiency of these shoots, although growing on 100 μg/ml kanamycin, was lower than the secondary shoots that develop from the tubers after 2-3 subcultures in MS 31 (Table 1).

Apparently, the placement of tuber discs on auxin containing media breaks the bud dormancy and shoots emerge from already existing primodia. These shoots were unable to root in media containing 100 μg/ml kanamycin. After the primary shoots were excised, tuber discs formed callus, and new shoots developed through *de novo* meristematic tissues within the calli.

Regeneration efficiency (number of regenerated shoots / number of explants) was higher in Desirée than in the other cultivars tested. The efficiency of regeneration is in the following order: Desirée > Shepody > Russet Burbank > Bintji. The number of shoots regenerated from each individual explant was also higher in Desirée, i.e., between 2-5 shoots developed from some tuber discs, but only one shoot / disc was retained to ensure that each of the shoots tested is a result of an independent transformation event and clonal in origin.

Efficiency of regeneration through stem explants was higher than the tuber, in both Shepody and Russet Burbank (Table 1). However, this system of transformation produced more escape shoots (non-transformed kanamycin sensitive) than tuber transformation on the basis of their ability to root and plant survival on 100 μg/ml kanamycin. During the first culture period 20-30% of the explants regenerated shoots. However, none of these shoots rooted in media containing 100 μg/ml kanamycin (Table 1). The secondary shoots regenerated through callus after removing the first shoots and successfully rooted on media containing 100 μg/ml kanamycin. Both transformation protocols used in this work resulted in morphologically normal shoots. Transgenic potato plants of all the four cultivars tested appeared normal and their morphology, growth characteristics and number of seeds were identical to their non-transformed cultivars.

Expression of PVX coat protein in transgenic plants:

The transformation of potato cultivars with the Polyrok I containing the PVX CP resulted in a total of 40 kanamycin resistant plants. All transgenic plants were analyzed by Western blotting for the expression of capsid protein. Eleven lines were found to accumulate detectable amounts of PVX CP (fig. 2). The accumulated level of CP ranged between 0.02 - 0.06% of extracted total plant proteins. Protein extracts from the four transgenic cultivars and from untransformed Russet Burbank, Shepody, Desirée and Bintji were run on SDS - polyacrylamide gel and probed with anti-PVX IgG (Fig. 2). By comparison with purified PVX CP standards, several plants showed bands corresponding to PVX CP.

Analysis of PVX CP accumulation in different leaves of transformed plants and in different plants originated from micropropagation of one original clone showed that the expression was independent of the leaf age (results not shown) and did not show any detectable somaclonal variations (e.g. clones 304 in panel A (fig. 2) are 2 different plants derived from a single clone). Furthermore, when potato seeds of the original 304 clone were grown, for the second time, and leaves were analyzed for the expression PVX CP, again measurable amounts of CP were detected.

Resistance of transgenic potato plants to PVX:

Transgenic potato cultivars and untransformed controls were challenged with 90 μg of PVX per plant. After 15 days infection under green house conditions, six grams of potato leaves were randomly picked from infected plants and used as an inoculum on the PVX local lesion host Gomphrena globosa. Results shown in Table 2 indicate that transgenic potato cultivars are quite resistent to PVX infection in comparison to non-transgenic controls.

DISCUSSION

In this report we describe the introduction of resistance to PVX in several economically important potato cultivars. The CP of PVX was transferred into Russet Burbank, Shepody, Desirée and Bintji. The transformation protocol used resulted in morphogically normal shoots which gave rise to transgenic plants which are visually and morphologically indistinguishable from the untransformed plants grown under the same conditions. Potato is know to be extremely sensitive to somaclonal variation in tissue culture[22,23]. The lack of somaclonal variations in our transgenic plants is probably due to the low concentrations of growth regulators used during transformation and regeneration. Our results show that the primary shoots that regenerated from stem explants and the majority of those regenerated from tuber discs were not transgenic. Transformed shoots were recovered mostly from green callus proliferated from both stem explants and tuber discs. It is likely that cells at the cut surface of the explant pass through a period of dedifferentiation which make them permissive to transformation by agrobacterium. There are some persistent bacteria which stay on the explant after transformation. These bacteria could only be detected if carbenicillin was omitted from the media. It appears that these resistant bacteria are those that actually achieve transformation of newly dedifferentiated cells[24].

PVX capsid protein was produced in detectable amounts by Western blotting in about 50% of Desirée, 35% of Shepody and 25% of each Russet Burbank and Bintji plants. This result indicates that Desirée is more amenable to transformation than the other cultivars. The lower frequency of CP expression in the kanamycin resistant plants is probably due to either expression below our detection method or to the rearrangement, deletion of T-DNA[25]. The CP-mediated protection studies in other plant systems have reported that reduced levels of virus titer in transgenic plants relative to the corresponding non-transformed control plants[8]. We have reported that, under growth chamber conditions, transgenic potato cultivars showed much lower levels of PVX in the systemically infected leaves in comparison to the controls (Table 2). These results indicate that viral replication and/or transport of the PVX is inhibited in some way due to the presence of the viral CP. It is possible that the uncoating of the incoming virus is inhibited or the CP is competing with the virus for an attachment site.

ACKNOWLEDGEMENTS

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Table 1: Transformation / Regeneration efficiency of different potato cultivars

Cultivar	Explant origin	Primary Regeneration 1st Culture				Secondary Regeneration 2nd Culture			
		* Culture efficiency	+ Total No of Shoots	% Rooted Shoots	% Cp+	* Culture efficiency	+ Total No. of shoots	% Rooted Shoots	% Cp+
Desiree	TD	20/100	ND	70	10	40/60	50	50	50
Shepody	TD	13/100	15	30	ND	25/70	27	ND	ND
Shepody	S	30/95	33	0	0	34/70	40	90	33
Russet / Burbank	TD	9/100	13	25	ND	20/75	28	95	25
Russet / Burbank	S	28/100	33	0	0	30/60	34	95	28
[illegible]	TD	3/100	6	ND	ND	15/30	ND	ND	35

TD: Tuber Disc. S = Stem ND = Not Determined CP = Coat Protein

* Culture efficiency = number of explants regenerated / number of explants cultured

+ Total number of shoots is higher than the number of regenerated explants because there were more than one shoot per transformed explant. However, only one shoot / per explant was used for rooting and further testing.

TABLE 2: Local Lesion assay showing the accumulation of PVX in potato leaves of non-transformed and transgenic cultivars.

Dilution*	Exp. #1 Transgenic	Exp. #1 Non-transformed	Exp. #2 Transgenic	Exp. #2 Non-transformed	Exp. #3 Transgenic	Exp. #3 Non-Transformed
	# of local lesions					
1:1	2	20	4	41	4	20
1:2	1	24	1	19	1	6
1:4	0	0	1	8	0	3
1:8	0	3	0	2	0	1
1:16	0	0	0	1	0	0

*Two grams of leaves were ground in 3 ml Tris-HCl buffer pH 7.5, and diluted with the same buffer prior to inoculation of five leaves of Gomphrena globosa.

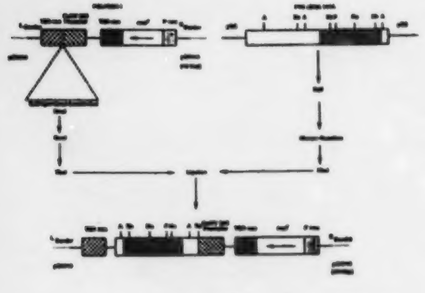

Figure 1 Schematic representation of the arrangement of PVX coat protein cistron (CP) in the [illegible] vector [illegible]. Plasmid was digested with [illegible] and [illegible] between the CaMV 35S promoter and nos terminator. PVX cDNA clone [illegible] was first digested with [illegible] and then treated with Klenow fragment to render this end blunt. Subsequent digestion with [illegible] and ligation prior to transformation to Agrobacterium tumefaciens (LBA 4404).

A)

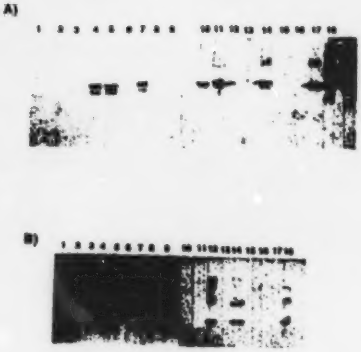

Figure 2 Western blot analysis of PVX CP expression in transgenic potato plants. Proteins (15 µg) were extracted from leaves and separated on a 12% SDS-PAGE.

(A) Lane 1: [illegible] proteins of control (untransformed) Russet Burbank. Lanes 2-10: Transformed calluses of Russet Burbank giving rise to the following transgenic clones [illegible] in lanes 4, 5, 7 and 10 respectively. Lanes 11-14: Transformed Shepody clones giving rise to [illegible] in both lanes 13 and 14. Lanes 15-17 clones of Russet Burbank [illegible]. Lane 18 corresponds to 2 µg of PVX CP control.

(B) Lane 1: Control as in A. Lanes 2-11: Transformed calluses of Desiree giving rise to transgenic clones [illegible] in lanes 5, 7 and 9 respectively. Lanes 12 and 13 transformed Russet Burbank. Clone [illegible] in lane 12. Lanes 14-17: Transformed calluses of [illegible] giving rise to transgenic clone [illegible] in lane 14. Lane 18 corresponds to 2 µg of PVX CP control.

VOLUME II

SESSION G

TECHNOLOGIES/BIOTECHNOLOGY

POSTER PRESENTATIONS

GP1

DEVELOPMENT AND VALIDATION OF A NEW, RAPID, AND ECONOMICAL SURROGATE BIOASSAY FOR INDUSTRIAL CONTAMINANTS.

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1.0 INTRODUCTION

Bioassays have been applied to numerous organisms representing different trophic levels in the aquatic food chain, including fish, arthropods, algae and bacteria. Nevertheless, the most widely-used type of procedure is the traditional acute bioassay, in which the lethality of various concentrations of a toxicant or toxicant mixture are measured within a predetermined exposure time. Standardized static bioassays, such as those using fish and crustaceans, have been and continue to be used extensively by regulatory agencies (e.g., Ontario Ministry of the Environment) in order to determine the potential effects of toxic materials. Although these tests yield quantitative measures of contamination levels, they are often either time-consuming, labour-intensive, or costly. In a review article over a decade ago, Sprague (1976) suggested that tests on lower levels of the food chain (i.e., invertebrates and algae) yield a great deal of useful data, are rapid and efficient, and, most importantly, often give results comparable with traditional bioassays using fish.

In light of these points, and the movement towards a "battery of tests" toxicological approach, there is a continuing need for the development of predictive dose-response relationships for aquatic organisms, emphasizing "lower" trophic levels. One of the main advantages of this is that organisms "lower" in the food chain may act as early warning indicators for more significant adverse effects on "higher" level food chain biota such as fish, birds, and mammals. This may be especially important where chronic toxicity is a factor.

Ciliated protists are unicellular aquatic microzooplankton which feed predominantly on bacteria and small phytoplankton. They are important organisms in the transfer and transformation of nutrients in both marine and freshwater food chains (Beaver and Crisman 1989, Pace and Orcutt Jr. 1981). Recently, with a movement in toxicological research towards (a) more rapid assessment techniques, and (b) indicators of chronic, sublethal effects of toxicants in fresh water, many investigators have turned to ciliated protists (and other aquatic microbes) as test and/or indicator organisms for the assessment of eutrophic and polluted waters, since they have been shown to be sensitive to a variety of toxicants present in the natural environment.

This study specifically addresses the development and reliability of a new protistan bioassay technique for monitoring the toxicity of pure compounds and industrial effluents. The sublethal bioassay technique utilizes the chemotactic responses of the ciliated protist, *Tetrahymena vorax*, as an indicator of aquatic toxicity.

2.0 MATERIALS AND METHODS

The approach used in this study was first to develop a protocol for a sublethal toxicity bioassay using, as an indicator, the chemotactic response of the ciliated protist, *Tetrahymena vorax*. Second, the protocol was applied to standard reference toxicants, commonly used with other standard bioassays (Environment Canada 1990). The third and final phase involved testing the protocol with toxicant mixtures (effluents) from several industries, namely, Pulp and Paper, Metal Casting, Iron and Steel, and Organic Chemical. During this final phase, two other standard OMOE bioassay protocols (*Daphnia magna* 48-hr acute lethality test, Poirier *et al.* 1988; rainbow trout 96-hr acute lethality test, Craig *et al.* 1983) were also implemented using the same effluents. This allowed for comparison of the ciliate protocol to the standard assays in order to understand the relationships between the respective bioassays and to determine the utility and feasibility of the new ciliate bioassay, in light of standard test results.

Protocol Development

The goal of the first phase of the study was to establish cultures of the test organism, *Tetrahymena vorax* and to develop a working protocol (T-Maze Toxitactic Assay (TMTA)) with which reference toxicants and effluents could be tested, in order to evaluate the utility and feasibility of the protocol.

Implementation of Reference Toxicant Tests

Reference toxicants were chosen in conjunction with the Ontario Ministry of the Environment. Reference toxicant tests were implemented with the TMTA, for two important reasons: (i) to determine estimates of concentrations with which tests should be run for given classes of toxicants (i.e., heavy metals, organics, etc.); and, (ii) to compare these results with those of other standard bioassays using similar reference toxicants.

The tests were carried out with four different reference toxicants, commonly used for similar purposes for other toxicity bioassays (Environment Canada 1990). The reference toxicants tested in this phase of the study were: zinc, 4-chlorophenol, sodium chloride, and cadmium. The first three reference toxicants were chosen for comparability to data from bioassays with other taxa (i.e., *Daphnia magna*, rainbow trout tests), while the fourth toxicant, cadmium, was tested for comparability to data from another ciliate protocol using chemotaxis as the test parameter (see Berk et al. 1985).

Implementation of Effluent Tests

For each effluent sample used in this phase of the study, a split sample was used to run the TMTA protocol using at least five concentrations and a control (with replication). The rest of the sample was used to carry out the standard OMOE protocols with *Daphnia magna* and rainbow trout. The TMTA test was always run concurrently with these two other tests.

3.0 RESULTS AND DISCUSSION

Protocol Development

Cultures of the test organism were established successfully and maintained throughout the duration of the study. The protocol development phase yielded positive results, as indicated by: tests with a T-maze rack, designed to eliminate biases due to gravity; clonal age tests, implemented in order to determine the age of cells in exponential phase of growth; and, control tests, designed to determine the precision and rigour of the test itself.

The aspects of the protocol requiring refinement are: (a) the treatment of cells prior to the initiation of the test; and (b) the possible use of different species as test organisms.

Reference Toxicant Tests

Tests were implemented with four reference toxicants. Using the TMTA, the only reference toxicant that yielded a significant LOEC value was sodium chloride. In this preliminary testing, it appears that the test, implemented with standard reference toxicants, is not sufficiently sensitive (in relation to other standard tests), although pre-treatment of cells through the use of a starvation buffer may yield more promising results (see Roberts and Berk 1990). Previous ciliate toxicity data using chemotaxis as the test parameter, and heavy metals as test toxicants (Berk et al. 1985) indicates that ciliates may respond sublethally in a similar range as *Daphnia* and trout do in acute lethality tests. Results from other ciliate toxicity tests are based on slightly longer response times (i.e., growth rate) or utilize direct physiological parameters (i.e., respiration) and so are not strictly comparable with this protocol, since it utilizes a test parameter that relies upon a relatively rapid behavioural response on the part of the organism.

Effluent Tests

TMTA tests were implemented with effluents from several industrial sectors. Using the test, the majority of effluents generally had little effect on the chemotactic response of the ciliates. Only 4 out of 11 effluent tests yielded results comparable to results from acute lethality tests. Interestingly, these similarities were observed with effluents from the pulp and paper sector only. It is possible, therefore, that the test may prove useful specifically for pulp and paper effluents.

There are several reasons why results from tests using whole effluents would be problematic: (1) a given effluent is made up of more than one toxicant, often acting in a complex series of relationships (that have only recently begun to be understood); and, (2) effluents are not consistent from one sampling to another due to the heterogeneity associated with effluents from different industrial processes. Since there are no comparable data published that used ciliates as test organisms, and whole effluents as test toxicants, it is difficult to evaluate the potential success of this test protocol without further study.

* * *

Results from many recent toxicological studies with ciliated protists used as test organisms have already demonstrated that these protists can be effective bioassay organisms (Berk *et al.* 1985, 1990; D[illegible] and Leclerc 1975; Slabbert and Morgan 1982). Nonetheless, most of these studies used single toxicants in their evaluation of toxicity. To our knowledge, this is the first study of its kind testing whole effluents (with mixtures of potential toxicants) with ciliates as test organisms. It is not surprising, then, that there are problems and issues that arose in this study which require further resolution.

4.0 FUTURE WORK

A number of important issues for future research relating to the bioassay development emerged from the results of this study. Further work in developing this bioassay should be continued. A number important refinements to the protocol should be considered: (1) exploring variation in the preparation of cells used in the test protocol; (2) exploring reasons underlying test variability and providing some possible solutions; (3) implementing the test with other ciliate species (other than *Tetrahymena vorax*); (4) calibrating the test through an interlaboratory comparison; and (5) varying the exposure time.

5.0 LITERATURE CITED

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Computer - Controlled Batch Hydride Generator

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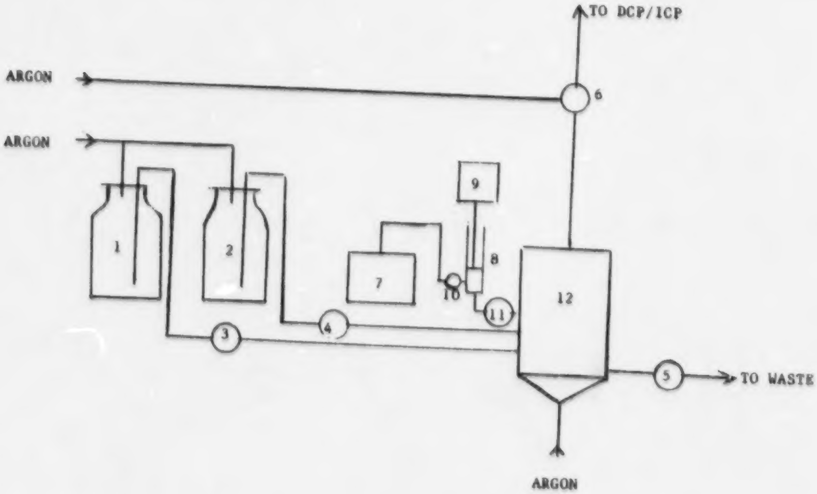
There are a number of advantages in the determination, by atomic spectroscopy, of those elements that can easily be transformed into gaseous compounds. Most important among these is the potential to transfer close to 100% of the analyte from the sample solution to the atom cell (flame or plasma). Elements that have ben determined this way by forming the hydride include arsenic, antimony, bismuth, germanium, tin, lead, selenium, and tellurium. By these means, the detection limits for these elements by hydride generation is much lower, sometimes as much as two to three orders of magnitude. Although the batch process was originally the method of choice for the determination of hydride-forming elements, it has become more common to use a continuous hydride generator to eliminate the problems created by operator error in performing the various mechanical functions required in the manual batch process.

Thus the maximum potential of the hydride method has been compromised by approximately an order of magnitude in order to achieve better reproducibility. In this work we have attempted to restore the advantage of the batch system without compromising on the detection limits. The functions of the operator have been taken over by a computer which provides consistent performance in the complex series of operations of the batch system.

Samples will be placed in a Gilson 212B sampling system. Via a system of valves and a syringe, an aliquot will be delivered to the reaction vessel/gas-liquid separator. Borohydride will be delivered to the vessel from a pressurized bottle. The transient signal produced in the plasma will be captured (8000 points), a Kalman Filter programme of our own design will be used to determine the peak height and area. These will be used to calculate the concentrations in the sample. A 386 computer is required here to provide sufficient calculating speed so that the computation is not the limiting step in the sample throughput rate.The raw data will be dumped, in preparation for the next sample. The reaction vessel will be drained and rinsed with a solution from a pressurized bottle. The tubing and the syringe containing the sample residue will be rinsed and primed with the next sample.


TO DCP/ICP
ARGON
ARGON
6
1
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11
12
5
TO WASTE
ARGON

COMPUTER CONTROLLED BATCH HYDRIDE GENERATOR

1. Rinse solution; 2. Sodium borohydride solution;, 3,4,5, 10, 11. Solenoid valves;
6. Three-way solenoid valve; 7. Gilson 212B Autosampler; 9. Syringe driver;
12. Reaction vessel/ gas liquid separator

A New Design of an *In-situ* Separator for Continuous Hydride Generation:

Application to On-Line Pre-reduction of Arsenic(V) and Determination of Arsenic in Water by Atomic Emission Spectrometry

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The continuous hydride generator is one of the systems used for the spectrometric determination of hydride forming elements. In this system, the acidified sample and sodium tetrohydroborate(III) solutions are continuously pumped into a reaction coil where the analytes react with the reductant to form hydrides. The mixture of hydride and waste solution is transported into a gas-liquid separator, where the hydrides, released from the waste solution, are mixed with the carrier gas. Hydrides are carried into either the absorption cell for AAS or the plasma for AES where they are determined. Various types of gas-liquid separators, such as a U-tube separator, a packed U-tube separator, a porous membrane separator, and a porous tube separator, have been developed. Most of these separators were designed for generation of hydrides from concentrated acid media ($[H^+] > 2M$). The hydrides are stripped from the solution by the large amount of hydrogen which is generated by the reaction between tetrahydroborate(III) and acid. If hydrides are generated from a solution with low acid concentration, the efficiency of these separators would be low, owing to the small quantity of hydrogen produced.

In our previous work, we have reported methods to generate SnH_4 and AsH_3 from low acid media (0.01-0.04 M) by means of a batch hydride generator system. In these systems, L-cysteine and L-cystine played an important role to increase of reaction rate and the sensitivity, and to decrease interference from transition metal ions, and on pre-reduction of As(V) to As(III). Compared with the continuous system, the batch system can achieve lower detection limits but it is difficult to automate and requires the operator to be well trained.

To adapt the low acid L-cysteine system to fit the continuous hydride generation system, the development of a gas-liquid separator, which works in low acid media, was necessary. Based on the idea of the hydride generator used in the batch system, an *in situ* hydride generator/separator, in which the hydrides are not only generated, but also continuously separated from the reaction solution, has been designed and tested. This paper presents the design and characteristics of the generator and its application to the determination of arsenic.

The Design of Hydride Generator

An efficient hydride-generator should meet the following requirements: efficient mixing of the sample and reducing solutions for maximum yields of hydride; complete separation of the hydrides from the waste solutions; smooth transportation of the separated hydrides and the waste solution to the plasma and to the drain, respectively.

Based on these requirements and the chemistry of the process of hydride generation, the continuous hydride generator was designed. Sample and sodium tetrohydroborate(III) solutions are continuously pumped into the hydride generator/separator. The reactants meet and drop into the bottom of the vessel. The argon flow introduced into the generator through a glass frit at the bottom of the vessel produces fine bubbles, which not only violently mix the solution but also provide a large gas-liquid interface area to promote the hydride's being stripped from solution. To increase the total flow rate of the carrier gas, another flow of argon is introduced into the vessel from the top. The two flows of argon mix and sweep the hydrides into the plasma through the outlet port. The waste solution is pumped out to the drain. The gas/liquid separator is made wider at the top to minimize the likelihood of bubbles reaching the transfer line to the plasma.

The system has been used for the determination of arsenic, germanium, and selenium, using a direct-current plasma atomic emission spectrometer as a detector. Detection limits were found to be 4, 0.3, and 8 ng ml^{-1} for arsenic, germanium, and selenium, respectively. In studies of interference from several of the most strongly interfering elements, the continuous hydride generator, provided superior performance over the batch process, when L-cysteine was incorporated both to reduce arsenic(V) and to reduce interferences from transition elements. Also, this technique provided significantly superior results to the conventional high acid hydride generation method.

The method has been applied to the determination of arsenic in water samples from the Ontario Ministry of the Environment. Good agreement has been found between samples analyzed by inductively coupled plasma mass spectrometry and the technique that is described.

Acknowledgement

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OP4

BASIC AND APPLIED STUDIES
WITH A
TRACE ATMOSPHERIC GAS ANALYZER
TAGA 3000

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The SCIEX TAGA series of mass spectrometers utilize an atmospheric pressure ionization (API) source. The technique of API mass spectrometry was introduced as an analytical technique by Carroll *et al.* [1]. Because of its high sensitivity towards trace compounds in air, API has since developed into a mass spectrometric technique in its own right [2]. In addition to the monitoring of trace organic compounds in ambient air, API has found analytical application as an interface for liquid chromatography/mass spectrometry (LC/MS). Our objectives have been to establish a collaborative research facility, using the TAGA 3000, at Trent University and to study the gas-phase ion/molecule reactions which occur in the API source and which may help improve the sensitivity of the instrument to a variety of compounds.

The TAGA 3000 API source is depicted schematically in Figure 1.

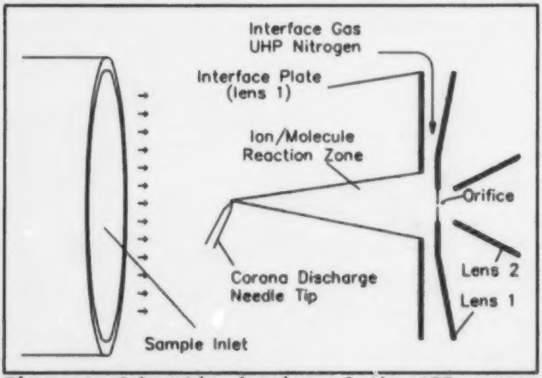
Interface Gas
UHP Nitrogen
Interface Plate
(lens 1)
Ion/Molecule
Reaction Zone
Orifice
Corona Discharge
Needle Tip
Lens 2
Lens 1
Sample Inlet

Figure 1. Schematic drawing of the API source utilised by the TAGA 3000 analyser.

The API source utilizes a high voltage corona discharge between the needle tip and the Interface Plate and draws a current of 2 μA typically. Electron ionization of the major gases in the air stream (N_2 and O_2) initiates a sequence of ion/molecule reactions that results, in a few microseconds, in the formation of hydronium ion-water clusters ($H_3O^+(H_2O)_n$; $n=0,1,\ldots$). These clusters undergo successive collisions in the source and an equilibrium is established such that, at 25°C with 5 Torr partial pressure of water (relative humidity 21%) the majority of clusters contain *ca.* 5-8 water molecules [3]. These hydronium ion-water clusters are the main reagent ions in API and they can protonate, through collision, molecules (B) whose gas-phase proton affinity (PA) is higher than that of the protonating cluster.

The proton transfer reaction is represented in reaction (1):

$$AH^+ + B \rightarrow BH^+ + A \qquad (1)$$

where:

A represents a gas-phase Lewis acid (proton donor)
H^+ represents the proton
B represents the target analyte (proton acceptor)

The magnitude of the enthalpy change (ΔH) associated with this reaction is referred to as the proton affinity (PA); another term which is often associated with reaction (1) is the free energy change (ΔG) or gas-phase basicity. The proton affinities of some compounds of interest are shown in Figure 2.

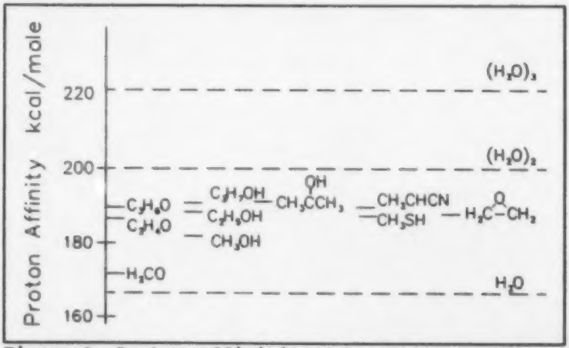

Figure 2. Proton affinities of some compounds of environmental interest.

Real-time detection of some classes of compounds in air has been a long-standing problem with the Trace Atmospheric Gas Analyser (TAGA). As the proton affinities of numerous low-molecular-weight aldehydes and alcohols are not much greater than that of water, the process of proton transfer does not occur readily in the API source of the TAGA. Furthermore, the difficulty in protonating the analyte is increased by the fact that the proton affinities of water clusters increase with increasing number of water molecules.

The specific reaction of protonation of B by water clusters is:

$$H_3O^+(H_2O)_n + B \rightarrow BH^+(H_2O)_x + (n+1-x)H_2O \qquad (2)$$

In the absence of hydration, proton transfer will occur at every collision for most compounds with PA higher than that of water; however, the presence of higher hydrates of water in the reagent ion composition results in a response of the instrument which may be divided broadly into three groups [4]:

i) K-group: When proton transfer occurs at every collision, the system is said to be under "kinetic control" of the production of analyte molecules and results in the maximum sensitivity towards a particular compound. Generally, oxygen bases which possess a PA of greater than *ca.* 200 kcal/mole have high sensitivities which are determined by fast kinetics for proton transfer from the reagent $H_3O^+(H_2O)_n$ ions.

ii) T-group: Most analytes with PA less than *ca.* 200 kcal/mole have sensitivities which are determined by the thermal equilibrium distributions of $B^+(H_2O)_n$ and $H_3O^+(H_2O)_n$; this condition is referred to as thermodynamic control.

iii) L-group: Sulphur and carbon bases have much lower sensitivities than are expected from their PA values. This decreased sensitivity derives from the relative instability of the protonated hydrates $BH^+(H_2O)_x$.

Thus a compound such as acetonitrile has a reasonably high sensitivity allowing for sub-ppb detection in ambient air, whereas another compound such as thiophene, with a similar PA, has virtually no sensitivity in the API source.

Methods for Increasing Sensitivity

1) adduct ion formation

Not only protons may be transferred to target analytes but also ions such as NH_4^+ and Cs^+ may add to target bases. We have produced Cs^+ and $Cs^+\cdot(H_2O)$ ions in the TAGA 3000 airstream *via* a novel atomizer source, but have not yet had success in improving the sensitivities for those compounds depicted in Figure 2.

2) selective ion/molecule reactions

We have attempted to react o-methylhydroxylamine with formaldehyde in the air stream of the TAGA 3000; the signal arising from the anticipated reaction product was not intense enough to improve the sensitivity of the instrument towards this compound.

3) temperature control of the reaction zone

Kebarle has reported surprising increases in sensitivity by heating the air stream. We are investigating this response of sensitivity to temperature as a means of controlling the rate of production of target analyte ions.

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Supercritical Fluid Extraction with Simultaneous Class Fractionation of PCBs and PAHs from Adsorbent Materials for Air Pollution Determinations

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Introduction

The Soxhlet leaching of adsorbent materials containing trapped organics, has traditionally been used for sample preparation for determination of trace contaminants in ambient air. This liquid extraction procedure is time consuming and create large amount of organic solvent waste. In the past few years, supercritical fluid extractions have shown excellent characteristics for rapid extraction of the organic contaminants from different matrices. In this paper, Supercritical Fluid Extraction (SFE) has been developed as an alternative to Soxhlet extraction for the determination of the trace organic contaminants in ambient air. In addition, PCBs and PAHs can be simply class fractionated when Florisil™ is used as a sorbent and by varying SFE conditions.

Experimental

The following materials were used for adsorbents in the extraction studies: Florisil™, 60/100 mesh, C18, XAD, Tenax™, Silica gel and Polyurethane Foam (PUF). Each adsorbent was cleaned by the Soxhlet method of extraction, with 250 ml of hexane for 20 hours. A standard hexane mixture was prepared containing selected PAHs and PCBs which are Acenaphthylene(ACE), 2,2',5-Trichlorobiphenyl(PCB3), 2,2',3,4,5-Pentachlorobiphenyl(PCB5), Benzo(a)anthracene(BEN), 2,2',3,4,4',5,6,6'-Octachlorobiphenyl(PCB8), Decachlorobiphenyl(PCB10), Indeno(1,2,3-cd)pyrene(IND), Coronene(COR), Benzo(g,h,i)perylene(BEP), and 2-Methyl-anthracene(Internal Standard).

SFE was performed with a high-pressure vessel which was constructed of stainless steel in the Science Machine Shop at the University of Waterloo. The vessel with a volume of 200 ml could withstand pressure in excess of 20000 psi. At the outlet of the pressure vessel, an extraction vessel consisted of two 1/4" to 1/16" reducing unions, 316 stainless steel fittings (Swagelok) and a 2.25" SS tubing. A 20 cm x 25 µm fused silica capillary was connected to the extraction vessel acting as a restrictor to maintain the pressure in the system. The capillary was directed into a 1.8-ml vial containing approximately 1.0 ml of hexane. The supercritical fluid sample was collected in the vial and concentrated to 100 µl with a gentle stream of nitrogen.

Three procedures were performed in the experiments. The first procedure was to determine which adsorbent would be the best to enable quantitative recoveries of all selected PCBs and PAHs from the matrices. Each adsorbent was spiked by injecting a small volume (100 µl) of standard mixture solution. The adsorbent in the vessel was then extracted with N_2O or N_2O with 6.5% by volume of modifier at 6000 psi for 30 minutes. The second procedure was to test the adsorbents' (XAD, Tenax™, Florisil™) ability to effectively contain trace organic contaminants during the adsorption and drying steps of the analytical process by spiking 100 µl of the standard mixture directly on top of the selected adsorbent in the extraction vessel, and passing moisture through the adsorbent for 24 h. Then the moisture was removed from the adsorbent by purging dry nitrogen through the extraction vessel for 30 minutes at 60°C. The saturated and dried adsorbent containing standard mixture was then extracted using N_2O with 6.5% by volume of modifier at 6000 psi for 30 minutes. The third procedure was to fractionate PCBs from PAHs by varying pressure of supercritical fluid N_2O.

A Varian 3500 capillary gas chromatograph, equipped with a splitless injector, a flame ionization detector (FID), and a 30 m x 0.25 µm fused silica capillary column (DB-5, J & W Scientific, California) was used for chromatographic analysis. The oven temperature was programmed to ramp from 140°C to 225°C at 15°/min, then to 300°C at 20°C/min and held there for 14 minutes. The FID temperature was set at 325°C. The temperature of the injector was set at 300°C.

Results and Discussion

Six commercially available adsorbents are evaluated for their ability of recovering contaminants. As shown in Table 1, all PCBs could be extracted quantitatively with pure N_2O. However, PAH compounds, particularly IND and COR were poorly recovered because of strong interaction of these large compounds with the matrix.

Table 2 shows the percentage recoveries of the standard mixture from the selected adsorbents using supercritical N_2O plus 6.5% by volume (100 µl) of methanol modifier. This method quantitatively recovered all compounds in the standard mixture from PUF, Florisil™, C18, Silica Gel, and Tenax™. The difficulties in recovering high molecular weight PAHs from XAD still remain. Table 3 shows the percentage recoveries of the standard mixture from the selected adsorbents using supercritical N_2O plus 6.5% by volume of toluene modifier. Similar to Table 2, this method can also improve the recoveries of IND and COR but in a lesser extend than using methanol modifier. Quantitative recoveries of all compounds from XAD are obtainable with this conditions. This may indicate that the energy barrier of desorption between the analyte and adsorbent can be reduced by selective interaction of aromatic ring in toluene with the matrix-solute complex since XAD resins also contain aromatic rings in their structure. For other adsorbents, the method involved toluene modifier results in lower recoveries.

Apparently, if XAD is chosen to be the adsorbent, the method using toluene modifier will be superior than other modifier while methanol is suitable for the other five adsorbents.

In air sampling, the trace organic contaminants along with moisture from the air are trapped in the adsorbent matrices contained in a cartridge. The moisture must be removed from the adsorbent to ensure successful SFE and gas chromatographic analysis. Three adsorbents (XAD, Tenax™, Florisil™) were investigated by comparing their

Table 1. The average recoveries for the extractions with pure N_2O at [illegible] psi and 40°C

Compound	XAD	PUF	Florisil™	C_{18}	Silica Gel	Tenax
ACE	111.3 ±3	94.2 ±1	78.4 ±6	86.1 ±6	69.3 ±1	87.1 ±0
PCB3	105.0 ±3	98.5 ±1	90.0 ±10	94.6 ±5	89.0 ±2	98.9 ±1
PCB5	94.8 ±5	91.9 ±0.3	89.2 ±1	90.2 ±3	90.3 ±1	97.0 ±1
BEN	96.8 ±2	90.5 ±1	71.1 ±6	93.1 ±2	108.5 ±2	90.1 ±2
PCB8	91.6 ±9	92.1 ±1	76.9 ±3	84.6 ±4	109.5 ±3	97.0 ±2
PC10	80.3 ±12	92.3 ±1	71.0 ±8	71.7 ±15	101.9 ±2	97.0 ±2
IND	76.4 ±13	83.0 ±3	45.0 ±5	75.7 ±14	88.0 ±9	84.0 ±3
COR	12.0 ±8	53.3 ±4	2.2 ±1	46.2 ±15	30.5 ±6	34.7 ±6

Table 2. The average recoveries for the extractions with N_2O + methanol at [illegible] psi and 40°C

Compound	XAD	PUF	Florisil™	C_{18}	Silica Gel	Tenax
ACE	109.1 ±13	92.3 ±2	86.7 ±3	89.0 ±2	112.8 ±10	86.4 ±1
PCB3	127.2 ±17	118.5 ±10	95.4 ±3	97.8 ±2	146.3 ±15	98.2 ±0.2
PCB5	102.4 ±6	119.8 ±3	91.1 ±2	98.7 ±4	126.9 ±8	100.9 ±2
BEN	64.8 ±19	96.8 ±4	130.0 ±2	97.9 ±7	133.2 ±4	100.3 ±0.3
PCB8	91.6 ±11	113.1 ±0	93.6 ±1	99.0 ±6	97.7 ±14	100.2 ±0.4
PC10	91.7 ±14	100.8 ±2	98.1 ±1	98.1 ±7	111.3 ±2	100.0 ±0.2
IND	63.4 ±1	108.3 ±11	92.6 ±1	100.3 ±13	152.5 ±15	98.3 ±1
COR	58.1 ±2	83.6 ±13	88.8 ±10	108.5 ±13	97.7 ±31	88.8 ±2

Table 3. The average recoveries for the extractions with N_2O + toluene at [illegible] psi and 40°C

Compound	XAD	PUF	Florisil™	C_{18}	Silica Gel	Tenax
ACE	87.3 ±4	66.0 ±1	74.0 ±11	62.5 ±23	63.3 ±6	73.1 ±2
PCB3	104.8 ±9	93.3 ±4	92.3 ±10	78.6 ±10	78.9 ±1	98.8 ±4
PCB5	94.8 ±7	91.5 ±2	86.6 ±9	71.3 ±2	73.9 ±3	89.9 ±4
BEN	98.3 ±8	83.4 ±37	97.0 ±16	74.4 ±3	75.0 ±1	94.4 ±8
PCB8	101.4 ±11	78.3 ±3	76.5 ±8	78.1 ±2	75.5 ±5	88.3 ±3
PC10	107.8 ±14	78.6 ±5	88.8 ±9	73.6 ±2	78.7 ±5	91.1 ±2
IND	98.8 ±5	45.9 ±9	81.2 ±20	88.8 ±4	88.6 ±3	94.2 ±3
COR	84.6 ±2	68.7 ±4	4.6 ±1	81.5 ±1	77.6 ±10	78.3 ±9

abilities to contain trace organic contaminants during adsorption, and retain those contaminants during the drying step.

Table 4 shows the average recoveries of components from saturated with moisture and then dried adsorbents. The following observations are made: the percentage recoveries for PCBs are generally good, being independent of the nature of adsorbents; the percentage recoveries for PAHs from XAD and Florisil™ are low compared to those obtained from previous experiments (the spiked standard mixture could be extracted quantitatively using N_2O with 100 µl of modifier at 6,000 psi and 40°C). There is no significant loss of analytes during the adsorbing and drying processes when Tenax™ is used as an adsorbent.

Table 5 shows the quantitative recoveries of target contaminants are obtained when the amount of toluene or methanol is increased from 100 µl to 150 µl or 200 µl (200 µl of toluene to XAD and 150 µl of methanol to Florisil™). This method significantly improves the recoveries of IND and BEP from the saturated, dried XAD or Florisil™.

It has been found that aging of XAD spiked with 100 µl standard mixture for 24 hours at room temperature lowers the percentage recoveries of all PAHs except acenaphthylene. Table 6 shows the comparison of percentage recoveries from aged XAD with the percentage recoveries from spiked XAD (Extractions were immediately done after a standard mixture was spiked onto the adsorbent). Spiked PAHs can be extracted quantitatively from XAD using N_2O with 100 µl of toluene since thermal energy easily overcomes the low energy barriers associated with weekly adsorption between the spiked PAHs and the matrix. In the case of saturated then dried PAHs, because of the aging of PAHs for 24 hours during saturating process, the desorption is more difficult, the PAHs become strongly adsorbed onto active sites of the adsorbent. In order to extract strongly adsorbed analytes which bond to sites of XAD or Florisil™, the

Table 4. The average recoveries of contaminants from saturated and dried adsorbents

Conditions SF: N_2O 6,000 psi 40°C 30 min	ACE	PCB3	PCB5	BEN	PCB8	PCB10	IND	BEP
Sat., dried XAD 100 µl of Toluene	85.2 ± 9.9	92.5 ± 4.9	101.2 ± 3.5	65.8 ± 20.8	109.0 ± 2.7	109.1 ± 3.4	8.9 ± 4.7	7.7 ± 2.4
Sat., dried Tenax 100 µl of MeOH	93.0 ± 0.4	97.3 ± 4.3	101.2 ± 5.5	80.5 ± 3.8	101.7 ± 2.4	98.4 ± 3.2	89.2 ± 9.4	84.0 ± 4.3
Sat., dried Florisil 100 µl of MeOH	68.7 ± 2.7	84.1 ± 0.6	89.4 ± 4.4	79.8 ± 2.0	85.5 ± 5.6	83.9 ± 9.8	72.2 ± 13.1	68.2 ± 13.6

Table 5. The percentage recoveries of contaminants from saturated and dried adsorbents using a large amount of modifier

Conditions SF: N_2O 6,000 psi 40°C 30 min	ACE	PCB3	PCB5	BEN	PCB6	PCB10	IND	BEP
Sat., dried XAD 200 µl of Toluene	87.2 ± 4.5	96.3 ± 5.2	104.1 ± 7.2	108.8 ± 11.9	108.5 ± 9.4	101.8 ± 6.9	96.3 ± 7.7	86.2 ± 5.7
Sat., dried Florisil 150 µl of MeOH	71.3 ± 3.5	90.4 ± 2.7	94.3 ± 4.6	78.9 ± 6.9	108.9 ± 33.6	87.9 ± 4.4	83.6 ± 8.1	82.8 ± 6.6

Table 6. Comparison of percentage recoveries from aged XAD with spiked XAD

CONDITIONS	ACE	PCB3	PCB5	BEN	PCB8	PCB10	IND	BEP or COR
Aged XAD for 24 h 100 µl of STD N_2O+100 µl of Toluene 6,000 psi 30 min 40°C	89.4 ± 16.2	106.1 ± 14.8	109.1 ± 13.4	58.6 ± 12.1	103.3 ± 10.7	98.5 ± 12.9	19.0 ± 4.1	16.5 ± 4.3
Spiked XAD 100µl of STD N_2O+ 100 µl of Toluene 6,000 psi 30 min 40°C	87.3 ± 4.0	104.8 ± 9.0	94.8 ± 7.0	96.3 ± 8.0	101.4 ± 11.0	107.8 ± 14.0	98.8 ± 5.0	84.8 ± 2.0

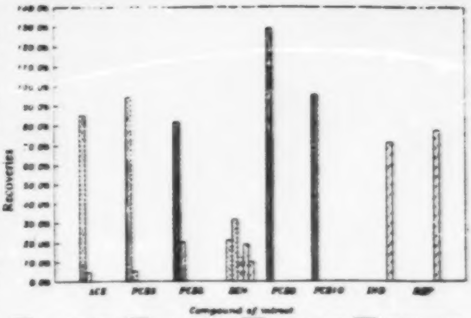
Table 7. Fractionation of PCBs from PAHs with Florisil™

Conditions	ACE	PCB3	PCB5	BEN	PCB6	PCB10	IND	BEP
N_2O 2,000 psi 25 Min 40°C	83.7 ± 1.3	92.0 ± 2.2	95.0 ± 6.7	0	119.1 ± 10.2	89.6 ± 6.0	0	0
N_2O/MeOH 6,000 psi 30 Min 40°C	2.2 ± 2.2	2.6 ± 2.6	10.6 ± 10.6	78.6 ± 15.2	0	0	73.8 ± 2.8	77.6 ± 0.8

amount of solvent to break the specific interaction between the target analyte and sorptive sites on the adsorbent, such as XAD, Florisil™, must be increased.

Five adsorbents were investigated to determine which would be the best adsorbent for fractionating PAHs from PCBs. The method can simplify the analysis of the complex mixtures and possibly remove the interferences from adsorbent in the air pollution studies.

Figure 1. The percent recoveries obtained by varying the pressure of the supercritical N_2O



Results obtained from XAD, Tenax™, C18, and Alumina show that these adsorbents cannot be used to fractionate PCBs from PAHs by varying pressure using N_2O or CO_2 since there is a large overlap between both groups. The Florisil™ is the best adsorbent providing fractionation of PCBs from PAHs. Quantitative recoveries of the PCBs were obtained from Florisil™ at 2,000 psi while 70 percentage recoveries of PAHs except ACE were extracted at 6,000 psi with modified N_2O (Table 7). This becomes evident when examining extraction pressure variation studies (Figure 1). The PCBs are quantitatively extracted with N_2O at 2,000 psi from Florisil™. BEN is partly extracted at 3,000 psi but it is not quantitatively recovered until the pressure of the N_2O is increased to 6,000 psi. IND and BEP are quantitatively recovered only at 6,000 psi with modified N_2O.

These results tend to indicate that the fractionation of the analytes from Florisil™ is based on the classes of compounds rather than on molecular weight. For example, PCB10 has a higher molecular weight (499) than indeno (1,2,3-cd) pyrene (276), and PCB10 is extracted at 2,000 psi with other PCBs rather than PAHs. The ACE is also removed with PCBs at 2,000 psi possibly due to its lower molecular weight and boiling point.

Currently our efforts are focused on replacing nitrous oxide with carbon dioxide when modifiers are used. Initial results indicate that similar recoveries are obtained, but the extraction times are increased by about 50 %.

Conclusions

Polychlorinated biphenyls and polycyclic aromatic hydrocarbons can be quantitatively recovered from adsorbents such as XAD resin, PUF, Florisil™ and Tenax™ with SFE. SFE with methanol or toluene will result in higher percent recoveries than the extractions without modifier.

During the adsorbing and drying steps of the analytical process, no significant loss of compounds contained on all adsorbents is found. However, an aging effect was observed, which requires the addition of larger amounts of modifier to obtain full recoveries.

Fractionation of PCBs from PAHs can be performed from Florisil™ using N_2O with MeOH as a modifier by varying the extraction condition.

SFE is an better alternative to Soxhlet extraction for the determination of trace organic contaminants in the ambient air, which significantly simplifies analyses and shortens extraction time by about an order of magnitude.

STANDARDIZED MATERIALS AND PROCEDURES FOR HEXAGENIA, A BENTHIC BIOASSAY ORGANISM: APPLICATION TO 21-DAY SEDIMENT BIOASSAYS.

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ABSTRACT

The comparability of sediment toxicokinetic, bioassay and biomonitoring studies is often limited because neither standard control sediments nor benthic test animals are readily available. We are developing and testing contaminant-free sediments and food supplements that promote rapid growth of Hexagenia mayflies, organisms recommended for use in sediment-bioassay and ecotoxicological studies. We have reared larvae from egg to maturity in as little as 3 mo.

Laboratory cultured animals and sediments were used in a serial dilution sediment bioassay of sediment highly contaminated with organochlorine compounds from the Detroit River (Trenton Channel). Large larvae were subjected to 21-d exposures of a sediment dilution series (1:0, 1:1, 1:3, 1:7, 1:15 or 0:1 mixture of Trenton Channel and synthetic sediment). Larval size was ascertained before and after exposure by measuring photographic images of individuals.

We detected no significant effect of the contaminated sediment on either survival or growth of Hexagenia. Variability among replicates and relative insensitivity of mature larvae to contaminants both contributed to this result.

Gas chromatographic analysis of contaminants in sediments and animals indicated significant compound-specific variability in dilution ratios and patterns of uptake. Ratios of concentrations of few compounds matched the nominal values expected as a result of dilution. Ratios for pentachorobenzene (QCB) and hexachlorobenzene (HCB) greatly exceeded the 16-fold difference expected in the 15:1 sediment mixture. Ratios for PCBs and other compounds ranged from 3-12. Different carbon species possibly influence binding capacity of the sediments. Uptake of QCB and HCB by Hexagenia decreased log-linearly among sediment dilutions, whereas levels of PCBs and other compounds were greatest in animals reared at intermediate (1:1 dilution) concentrations. Bioaccumulation factors varied greatly among sediment dilutions (6-20 in 1:15 dilution vs. 1.5-2 in 1:0 dilution). Feeding/metabolic inhibition or differential contaminant binding to varying carbon species are possible explanations.

Previously proposed sediment bioassay guidelines recommend control vs. treatment comparison of 21-d growth and survival of Hexagenia larvae, (10 half-grown individuals/2 L container, n=3 containers/treatment). However, such tests have limited statistical power: true differences between means $\geq 50\%$ and coefficients of variation $\leq 20\%$ are required for treatment effects to be judged significant at $p<0.05$ in 80% of experiments. At least 5 replicates should be used in 2-sample sediment bioassays.

A serial dilution bioassay permits evaluation of relative toxicity of bulk sediments analogous to procedures used for water bioassays. Additionally, gas chromatographic analysis of larvae and sediments from various dilutions can provide important information on variation of bioaccumulation factors with respect to sediment contaminant levels.

1. INTRODUCTION

Various bioassay and biomonitoring techniques assume that variation in test organism survival, growth and/or ultimate contaminant burden directly reflect the concentration and toxicity of contaminants in the sediment. Response differences between contaminated and uncontaminated site-collected treatments is assumed to reflect the influence of the contaminants alone. We have proposed that comparing both field-collected reference and contaminant-influenced treatments with a standard, laboratory-prepared control permits one to ascertain those test organisms' responses to on-site sediments that result from inappropriate or suboptimal physical sediment characteristics (Ciborowski and Corkum 1989).

We have been evaluating the utility of synthetic sediment as a reference (control) substrate in short- and long-term sediment bioassay procedures using *Hexagenia* mayfly larvae. *Hexagenia* larvae are important field and laboratory test organisms that have been recommended as a standard for evaluation of toxic effects of contaminated sediments (International Joint Commission 1987, Lomas and Krantzberg 1988). In this paper we report on; a) 21-day larval growth and survival; b) 21-day patterns of contaminant transfer; and c) the statistical power of bioassays that employ various levels of replication.

2. METHODS

2.1. Sediment Collection and Preparation

2.1.1. Contaminated Sediment

In June 1991, surficial sediment (top 7.5-10 cm; water depth 1-1.5 m) was collected with a metal bucket from the Trenton Channel of the Detroit River (42°15'N, 83°10'W; site 107 of Furlong et al. (1988)). The sediment was stored refrigerated in 8-L hexane-rinsed galvanized buckets until required. Sediments from this area are highly contaminated with organochlorine compounds (Thornley and Hamdy 1984; Furlong et al. 1988).

2.1.2. Synthetic (STND) Sediment

Our synthetic standard reference sediment (STND) consisted of a 21:21:16 ratio (dry mass) of silica sand (180-500 um diameter), prepared clay (Lewiscraft Sculptor's Clay®, Lewiscraft Ltd., Toronto, ON, M1S 2S2), and potting soil (Zehr's No Name Potting Soil®, Zehr's Ltd., Toronto, ON). The components were combined and dried prior to use according to procedures described by Hanes et al. (1990). The particle size distribution and organic content of this mixture are especially suitable for culture and growth of *Hexagenia* larvae. We have reared larvae from egg to maturity in this material in as little as 3 mo.

2.1.3. Experimental Bioassay Sediments

Dilutions of contaminated sediment were prepared by combining known proportions (by dry mass) of Trenton Channel sediment (loss on ignition (LOI) 10.6%) with STND sediment (LOI 8.4%). In July 1991, we produced 12 L of each of 6 mixture, designated 1X,0.5X,0.25X,0.125X,0.063X and 0X, where 1X represented 100% Trenton Channel sediment and 0X represented 0% Trenton Channel sediment (= 100% STND sediment). These corresponded to Trenton:STND ratios of 1:0, 1:1, 1:3, 1:7, 1:15 and 0:1, respectively.

Diluted sediments were prepared by measuring a required quantity of naturally wet Trenton Channel sediment into a container, stirring in STND sediment in dry form (<5% moisture), adding enough dechlorinated tapwater to produce a sediment of moisture content eqivalent to 1X sediment, and mixing thoroughly. All sediments were prepared on 5 July 1991.

2.2. Experimental Animals

The 21-day bioassay study was conducted with 120-day-old larvae (mean head widths among replicates 1.95-2.32 mm, mean body lengths 17.4-19.9 mm). Larvae had been hatched from eggs in the laboratory and mass-reared in STND-1 sediment on a diet of Tetramin® (Hanes et al 1990). On the first day of the study larvae were placed randomly in water-filled petri dishes (5 larvae per dish) whose bottoms had been marked with 1-cm lines. Each petri dish was photographed and the larvae were then transferred to a bioassay jar (10 larvae per jar) as required.

Jars were maintained, aerated for 21 d. Larvae were fed twice weekly with a 2 mL of a mixture of Tetramin®, baker's yeast and alfalfa powder (Hanes et al. 1990) to minimize effects of potential contribution of differences in edible organic matter to larval size/survivorship differences at the end of the experiment.

2.3. Bioassay Experiments

2.3.1. Experimental Procedures

The experiment was initiated in July 1991 following recommendations of Lomas and Krantzberg (1988) for 21-day in situ sediment assessment. Five replicate sediment samples of each treatment were prepared and placed within 2-L Universal glass jars (5 jars x 6 sediment types = 30 preparations). An equal volume of material (350 mL) was added to each jar to produce a sediment depth of 2 cm. Because Trenton Channel and STND sediments differed in density, wet masses differed slightly among treatments. Thirty identical preparations were made simultaneously for a long-term study (discussed elsewhere).

Following addition of sediment, dechlorinated tapwater was placed in each jar and lids were loosely put into place. Capillary tubing was inserted through the lid of each jar and below the water surface to provide aeration. Jars were kept at room temperature (20-22 $^{\circ}$C). Measurements of conductivity, pH and dissolved oxygen concentration indicated that all replicates had equivalent water chemistry at the beginning and end of the experiment (pH = 6.7, conductivity 390 uS cm^{-1}, oxygen saturated).

The experiment was terminated on 14 August 1991. We removed larvae while attempting to minimize disturbance to the sediments. Surface water was carefully poured off and replaced with carbonated water (club soda), which anaesthetizes larvae and causes them to rise to the water surface. All larvae from a jar were removed, placed into a gridded petri dish and photographed. Larvae were subsequently frozen and stored in hexane-rinsed jars prior to gas chromatographic (GC) analysis.

Aliquots of sediment from three randomly selected replicates of each of the sediments were placed in hexane-rinsed amber jars and stored frozen. Only the 0X, 0.063X and 1X sediment analyses have been completed to date and are reported herein.

2.3.2. Determination of Larval Growth

The size of each larva at the begining and end of the bioassay study was determined by measuring its photographic image (head width and body length) with reference to the size of the image of lines on the bottom of petri dishes in which the larvae were photographed. Head width provided less within-jar variation than body length. Thus, this variable was used to estimate larval growth. Growth was defined as the instantaneous percentage change in mean larval head width (100 x Ln(ratio of final: initial head width)) estimated over the course of the experiment. Larval growth has been measured for only the 1X, 0.063X and 0X treatments. Only these data are reported here.

2.4. Contaminant Analysis

Triplicate sediment samples and duplicate Hexagenia samples were analysed for organic contaminants concentration in the Great Lakes Institute analytical laboratory. Twenty-five-g aliquots of sediment were Soxhlet extracted for 24 h and analyzed according to the procedures described by Gobas et al. (1989). Hexagenia larvae (1.0-1.5 g wet mass composite from one bioassay jar) were homogenized with mortar and pestle and extracted by solid-liquid column extraction using 20 g anhydrous sodium sulphate and 300 mL 50% dichloromethane-50% hexane mixture as the solvent (Kovats and Ciborowski 1989).

Extracted samples were injected into a Hewlett-Packard model 5790A GC equipped with a 25 m x 0.25 mm fused silica column and an electron capture detector. Concentrations of 19 contaminants (14 PCB congeners, total PCBs, DDE, QCB, OCS, HCB, trans-nonachlor) were quantified based on peak patterns and comparision to those in standard mixes of known concentrations.

3. RESULTS AND DISCUSSION

3.1. Hexagenia Growth and Survival

Little mortality occurred over the 21-day interval of the study (Fig. 1A). One hundred percent survival was observed in at least two replicates of each treatment. Mean (±SE)

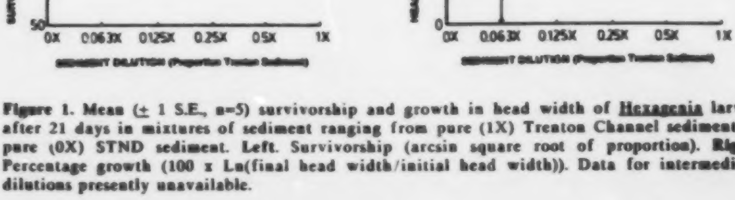

Figure 1. Mean (± 1 S.E., n=5) survivorship and growth in head width of Hexagenia larvae after 21 days in mixtures of sediment ranging from pure (1X) Trenton Channel sediment to pure (0X) STND sediment. Left. Survivorship (arcsin square root of proportion). Right. Percentage growth (100 x Ln(final head width/initial head width)). Data for intermediate dilutions presently unavailable.

Table 1. Mean (SE) concentrations of contaminants in sediments (left column, n=3) and *Hexagenia* (3rd column, n=2) from 0.063X dilution treatment, ratios of concentrations in 1X:0.063X treatments of sediment (2nd column) and *Hexagenia* (4th column), and *Hexagenia* bioaccumulation factors in 0.063X (5th column) and 1X (6th column) treatments.

Compound	Concentration in 0.063X Sediment (ug/kg carbon)	Ratio of Sediment Concentrations (1X/0.063X)	Concentration in 0.063X *Hexagenia* (ug/kg Lipid)	Ratio of *Hexagenia* Concentrations (1X/0.063X)	Ratio of HEX.:SED. Concentrations (0.063X)	Ratio of HEX.:SED. Concentrations (1.0X)
QCB	11.0 (3.6)	22.40	155.7 (10.3)	5.55	14.15	3.51
HCB	70.4 (19.2)	30.14	939.3 (119.1)	7.13	13.34	3.16
OCS	27.1 (2.5)	14.94	187.7 (16.4)	1.71	6.92	0.79
Trans-nonachlor	1.8 (0.9)	12.39	51.6 (2.2)	1.17	28.68	2.72
p,p'DDE	121.7 (8.0)	11.86	1786.0 (136.3)	1.91	14.67	2.37
PCB 28	34.4 (9.0)	3.41	217.0 (17.0)	2.29	6.31	4.25
PCB 52	104.8 (4.6)	5.66	1405.4 (87.5)	1.71	13.41	4.05
PCBs 66/95	129.2 (5.5)	6.21	1558.2 (230.6)	1.57	12.06	3.06
PCB 87	37.5 (1.2)	8.12	512.2 (38.6)	1.59	13.65	2.67
PCB 99	36.3 (0.7)	6.98	641.1 (63.5)	1.23	17.66	3.12
PCB 101	74.7 (2.1)	7.61	1162.5 (82.7)	1.61	15.56	2.88
PCB 110	66.8 (4.7)	7.75	859.8 (70.1)	1.72	12.88	2.85
PCB 118	66.1 (0.5)	7.85	924.7 (123.5)	1.65	13.99	2.58
PCB 138	107.6 (25.0)	7.75	956.6 (91.1)	1.40	8.89	1.6
PCB 153	44.3 (2.3)	10.59	678.7 (38.5)	1.21	15.31	1.75
PCBs 170/190	23.3 (4.3)	6.66	177.9 (13.0)	1.46	7.64	1.67
PCB 180	34.9 (0.3)	10.84	378.5 (7.8)	1.18	10.84	1.18
PCBs 182/187	20.6 (1.0)	11.56	211.7 (23.8)	1.37	10.30	1.22
PCB 194	6.6 (3.4)	15.78	133.2 (60.8)	1.20	20.33	1.54
Total PCBs	1468.5 (341.6)	7.83	13060.6 (1244.5)	1.40	8.89	1.58

among-replicate survival was lower in the 1X sediment treatment (86±5.1%, n=5) than in any of the other treatments (95-98%) but the difference was not significant (1-way ANOVA of arcsin square root transformed data, $p > 0.05$). Coefficients of variation (V) ranged from 11.9 to 18.7 percent.

Larval growth ranged from a mean loss of 3% of head width to an increase of 11% within individual jars over the duration of the experiment. Sexual dimorphism of larger larvae and an approach to emergence with consequent distortion of body dimensions contributed to size variability. There were no significant differences in mean growth among the 0X, 0.063X and 1X treatments, although growth appeared to be stimulated by pure Trenton Channel sediment (Fig. 1B; $p > 0.05$, Kruskal-Wallace test; coefficient of variation of Log transformed data ranged from 9 - 80%).

3.2. Contaminant Uptake

3.2.1. Sediment Contaminant Concentrations

Organic content of the Trenton Channel and STND sediments were comparable (10.6 and 8.4% at the beginning of bioassay). Food addition during the experiment increased organic content of the STND sediment by approximately 1.8 percentage points but did not influence organic content of the Trenton sediment.

Although the dilution of Trenton Channel sediment with STND sediment was expected to produce a proportional change in contaminant concentrations (16-fold between 1X and

0.063X), this did not appear to occur. The 1X:063X ratio of concentrations varied with individual compounds (Table 1). Pentachlorobenzene (QCB), hexachlorobenzene (HCB) and octachlorostyrene (OCS) ratios met or markedly exceeded expectations. Ratios for the remaining compounds were all <16. Ratios for PCBs ranged from 4-16 and tended to increase with increasing congener number. Because organic carbon content of STND and Trenton Channel sediments were very similar, ratios based on dry mass were almost identical to ratios based on carbon mass of the sediments.

We speculate that the noncongruence of ratios of individual contaminants between sediments may relate to qualitative differences in the organic carbon fraction of the two sediment types. We believe that the carbon species of STND sediment bound QCB and related compounds less tightly than the carbon species associated with Trenton Channel sediment. The contaminant dynamics only partly parallel patterns of contaminant hydrophobicity. Although values of the relatively soluble nonPCB compounds exceeded the expected 16-fold dilution ratio, ratios progressively increased with decreasing solubilities of the various PCB congeners.

3.2.2. Contaminant Uptake by Larvae

Larvae reared in reference (0X) sediment had very low but detectable concentrations of all contaminants assayed except OCS. Concentrations of QCB, HCB, OCS and trans-nonachlor were all <1.0 ug/kg wet mass. Concentrations of p,p'-DDE and 14 PCB congeners were all <2 ug/kg wet mass. Mean (±SE) total PCB concentration (expressed as Aroclor 1254/1260) was 21±(4.3, n=2) ug/kg wet mass. These concentrations are equivalent to or less than contaminant levels reported for larval and adult Hexagenia collected from 'uncontaminated' Ontario reference field sites (e.g., Bedard 1990, Kovats and Ciborowski 1989).

Patterns in contaminant uptake by Hexagenia with respect to specific contaminants paralleled the differences in concentration ratios between 1X and 0.063X sediment dilutions. Concentrations of QCB and HCB in Hexagenia increased approximately log-linearly with increasing proportion of Trenton Channel sediment (Fig. 2A). This pattern was evident for contaminant concentrations expressed both on a wet mass and a lipid mass basis, although lipid mass expression produced less variation among repli-

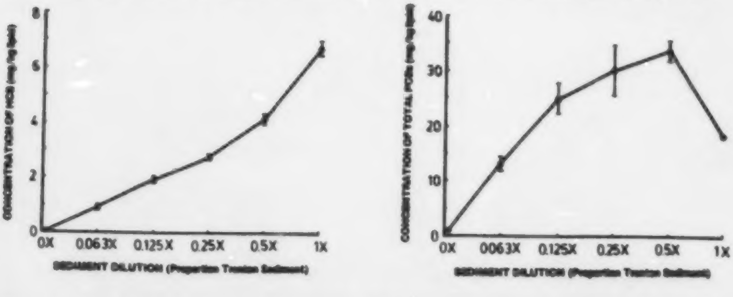

Figure 2. Mean (± 1 S.E., n=2) concentration of organic contaminants in Hexagenia larvae after 21 days in mixtures of sediment ranging from pure (1X) Trenton Channel sediment to pure (0X) STND sediment. **Left.** Concentration of hexachlorobenzene (mg/kg lipid). **Right.** Concentration of total PCBs (mg/kg lipid).

cates. Lipid comprised 1.3-2% of larval wet mass. Regression analysis revealed a significant positive relationship between *Hexagenia* concentration of QCB and HCB and Ln(Proportion of Trenton Channel sediment) ($F=255$, $p<<0.001$, $R^2=0.94$). However, there was significant deviation from linearity ($p < 0.005$). Concentration of PCBs increased log-linearly with increasing proportions of Trenton Channel sediment for all dilutions except the 1X treatment (Fig. 2B; linear regression analysis, $F = 24.45$, $p<0.05$, $R^2=0.84$). These findings are consistent with a differential uptake model of bioconcentration and bioaccumulation. Relatively soluble compounds (Log Kow<6.0) are thought to be taken up primarily by transport across respiratory surfaces, whereas ingestion pathways are more important for the less soluble compounds (Landrum and Poore 1988, Bedard 1990). We suspect that the reduction in PCB uptake in 1X treatments reflects a change in either feeding or physiological/metabolic behaviour of larvae. However, no significant differences in growth were found among treatments, so that these differences cannot be attributed to feeding rate per se. Accordingly, differential binding of contaminants to the carbon species present in Trenton Channel sediment is a more tenable explanation for these differences.

Variation in bioaccumulation ratios among sediment dilutions (Table 1) are also consistent with a hypotheses of reduced feeding or differential contaminant binding. Bioaccumulation factors (BAF) ranged from 6 - 30 (median 13.3) in 0.063X sediments but from only 0.8 - 4.3 (median 2.6) in 1X sediment. A decrease in BAF with increasing hydrophobicity among PCBs may indicate differences in the time required for the compounds to achieve equilibrium among sediment, water and mayfly larvae.

Although our bioassay failed to show significant mortality or growth effects of contamination on *Hexagenia*, contaminant transfer is obviously significant. Noncongruence in the behaviour of different contaminants at various dilutions has important implications for the evaluation and interpretation of bioassay results. There is clearly an interaction between contaminant characteristics and mode of uptake by larvae. The ultimate effect on BAFs and the organisms' success requires further study.

3.3. Statistical Power of Sediment Bioassays

Previously proposed sediment bioassay guidelines (Lomas and Krantzberg 1988) advocate comparison of 21-day growth and survival of *Hexagenia* larvae in triplicate samples of contaminated sediments to field-collected reference sediments. The ability to detect a significant effect (statistical power) depends on three factors: the true magnitude of the effect (D the difference between reference and treatment), among-replicate variability within treatments (expressed by the coefficient of variation V [100 x standard deviation/mean]) and the number of replicates per treatment (n). The power of a bioassay test is proportional to $(n \cdot D)/V$. If one wishes to be reasonably certain of detecting a specified difference D, (ideally defined by predetermined guidelines) then replication levels must be selected to accommodate the amount of among-replicate variability of the data.

Table 2 outlines the degree of replication necessary to provide 80% certainty of detecting a difference between two means (significant at $p < 0.05$) for different values of V and D. A bioassay test employing triplicate samples would be 80% certain to show a difference between two means of 50% if V was 20% or less (boldfaced entry of Table 2). Among-replicate variation in size and survival is often 30-50% or more for laboratory cultures of aquatic invertebrates such as *Hexagenia* (Hanes and Ciborowski 1991). Clearly, designs that employ triplicate samples of treatments are relatively insensitive. With 40% variation, growth or survival in controls must be almost almost half or double those in a treatment if an effect is to be judged significant in 80% of tests. We recommend employing a minimum of 5-6 replicates if differences as small as

Table 2. Minimum sample size necessary to be 80% certain that a specified true difference between two groups will be found significant ($p < 0.05$). V is the within-replicate coefficient of variation ($[s/\overline{X}] \times 100$). Line transecting table indicates minimum differences likely to be designated significant with triplicate sampling. Entries for which n>100 may be overestimated by approximately 2%. Three replicates are considered an absolute minimum sample size if outliers are to be identified. Entries were determined from power formulae given by Sokal and Rohlf (1981).

V(%)	TRUE DIFFERENCE BETWEEN CONTROL AND TREATMENT MEANS (%)									
	100	90	80	70	60	50	40	30	20	10
100	14	18	22	29	39	54	67	99	201	801
90	12	14	18	23	32	41	55	73	163	649
80	9	11	14	18	25	36	47	67	129	513
70	7	9	11	14	19	28	40	55	99	393
60	5	7	8	11	14	20	32	45	81	289
50	4	5	6	7	10	14	22	36	67	201
40	3	3	4	5	7	9	14	25	52	129
30	3	3	3	3	4	5	8	14	32	73
20	3	3	3	3	3	3	4	7	14	33
10	3	3	3	3	3	3	3	3	4	14

50% are to be judged significant (10-12 replicates x treatments in a two-sample study).

4. PROVISIONAL CONCLUSIONS

Simple sediment bioassays involving triplicate replicates of reference and treatment sediments are unlikely to have the power necessary to indicate toxicity except in extreme cases, especially if large, relatively tolerant mature animals are used. Replicated regression analyses are less powerful than two-sample comparisons if a fixed total number of observations is to be employed (Sokal and Rohlf 1981). However, designs such as the serial dilution protocol can provide important information regarding the dynamics of contaminant uptake. We recommend increased levels of overall replication be employed in sediment bioassays (a minimum of 10 observations among all groups/replicates), regardless of the design to be employed.

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QP7

DIAGNOSTIC EXPERT SYSTEMS: ENCODING CHEMICAL KNOWLEDGE IN AAdiagnosis

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Abstract This paper describes the design and implementation of a diagnostic expert system that is used to diagnose problems in the analysis for metals by atomic absorption spectrometry. In the AAexpert system, problems associated with instrumental analysis are classified into (a) problems that are detected during instrument optimization and (b) problems that are chemical in nature and are encountered only during sample analysis. The chemical knowledge is encoded at three different levels, namely (a) the primary level, (b) the secondary level, and (c) the tertiary level. A series of interconnecting rules are generated on compiling the secondary level of knowledge. The method of encoding chemical knowledge at three levels provides a robust technique which is generally applicable to encoding chemical knowledge for use in advisory expert systems.

ENCODING CHEMICAL KNOWLEDGE FOR AAdiagnosis

Our development project is part of a large, multi-component expert system named ACexpert, a system which is concerned with all aspects of chemical instrumental analysis (1). The expert system shell KDS 3 (from KDS Corporation, 934 Hunter Road, Wilmette, IL 60091, USA) has been chosen as the shell within which our expert system will be developed. The role of AAdiagnosis in AAexpert is to provide advice to users in areas related to diagnosing problems associated with the measurement of data. Through experiment, a series of unique symptoms that degrade the analytical quality of data obtained by flame atomic absorption spectrometry (AAS) have been identified (Table 1). Table 1 lists the symptoms (conditions) encoded in AAdiagnosis. In some cases the symptom can only be observed under special conditions. For example, when a sample is aspirated into the flame the real time signal from the photomultiplier tube exhibits a characteristic shape and noise when plotted as a function of elapsed time. Deviation from this signature can be used as a sensitive diagnostic tool.

We have evaluated the symptoms reported earlier (2, 3) and have adjusted the entries in the knowledge base to include additional symptoms associated with measurement of data by flame atomic absorption spectrometry. We find that analysis of information regarding noisy data requires certain instrumental set up and sample property information. These conditions have been incorporated into the knowledge base. The major causes of these symptoms have been deduced. The knowledge base of symptoms and causes and the resultant rule base is general for all flame AAS analyses and so these data can be applied to other systems.

In our approach we connect the instrumental set up conditions and sample chemical properties, to the analytical symptoms through logical relationships established at the primary and secondary level of knowledge development. The most important feature of any expert system is the construction of the knowledge base. Since the KDS knowledge base is represented as a matrix of facts we can build up information in three stages. The requirements to "fill in" the matrix leads in encoding the chemical information at three different levels, namely (a) the primary level, (b) the secondary level, and (c) the tertiary level (4). At the primary level, a condition is added to the knowledge base in order to discriminate between the existing knowledge. At the secondary level, the logical connections between conditions and case conclusions not related at the primary level are connected logically. Thus knowledge is represented in the form of a matrix of facts in which columns are represented by case conclusions and rows are represented by conditions. Table 2 shows the matrix of knowledge in AAdiagnosis. The knowledge in the matrix is said to be completely "filled" when the developer does not leave any condition unrelated with conclusions. The final level of expertise is added to the module when the developer encodes different combinations of symptoms that result in causes that exist in the knowledge base. These parallel cases added to the module depend on the previous experience of the expert.

DISCUSSION

Rule based expert systems have been widely adopted as a method of representing knowledge diagnostic expert systems. One of the best understood rule based expert systems in the field of analytical chemistry is the program for interpretation of infra red spectra (PAIRS) by Woodruff and Smith (5). This program was designed to aid the chemist in interpreting infra red spectra of liquid and solid samples. Changing or adding rules was not difficult but the drawback of the system was expressing chemical knowledge as well defined rules.

We have described a method of encoding chemical information for problems encountered during metal analysis by flame atomic absorption spectrometry. The constraints involved in adding new knowledge to an expert system based on conventional language led us to use of an expert system shell for the development of AAdiagnosis. We chose a rule based expert system shell that requires the chemical knowledge to be encoded in the form of case histories. AAdiagnosis treats the symptoms and the related causes as data. The primary level of knowledge relates symptoms directly with causes. The secondary level of knowledge relates symptoms with symptoms. The rules in AAdiagnosis are generated after compiling the secondary level of knowledge and therefore relate symptoms. The symptoms are universal and together with the causes represent our experimental results.

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Table 1. List of symptoms (conditions) in AAdiagnosis

1. Relative standard deviation of the measurements are high(>5%) and absorbance values are not precise.
2. Absorbance values are 50–80% of the expected values in the calibration graph.
3. Absorbance values are 20–40% of the expected values in the calibration graph.
4. Noisy absorption signal (observed from signal graphics).
5. Occasional pulse up or down in signal (observed from signal graphics).
6. Signal decays during absorption (observed from signal graphics).
7. Pulsating signal (observed from signal graphics).
8. The calibration graph levels off at high concentrations.
9. The calibration curve is sigmoidal.
10. There is a change in absorption sensitivity between re–calibration.
11. Drift in baseline.
12. The flame has a ragged appearance.
13. Bubbles form in the capillary tube.

Instrumental conditions that relate directly to the diagnostic rules:

14. Integration time is more than 3 seconds.
15. An oxidizing flame is being used.
16. Pressure is higher than 70 psi in the fuel cylinder.
17. The burner is set below 8 on the vertical scale.
18. A nitrous oxide–acetylene flame is being used.

Set up conditions that relate to the diagnostic rules:

19. A refractory element is present in the solution.
20. The samples are viscous.
21. The uptake rate is more than 5 mL/min.
22. Fluctuating display of lamp intensity while optimizing lamp.
23. The hollow cathode lamp is on but there is no display of lamp intensity while optimizing lamp.

	Contamination from samples	Improperly positioned glass bead	Burner rotated by 90 degrees	Scale expansion set too high	Contaminated spray chamber	Precipitation in the nebulizer	Incomplete mixing of sample & fuel	Too few atoms in the flame	Background absorption too high	Liquid build up-spray chamber	Burner slot blocked
DATA QUALITY CONTROL											
Relative standard dev high	T	T			T	T	T	T	T	T	T
Noisy absorption signal		T		T				T	T	T	T
Abs values 50-80%		T			T	T	T		T	T	
Drift in baseline										T	
Change in absorption sensitivity	T		T	T	T	T	T	T	T	T	T
Calbn graph levels off					T	T		T			
Abs values 20-40%			T					T			T
Calibration graph sigmoidal											
Flame - ragged appearance					T	T				T	T
Pulsating signal							T			T	
Bubbles form in capillary tube											
Occasional pulse	T				T						
Decaying signal						T					
INSTRUMENTAL CONDITIONS											
Pressure <70 psi											
Oxidizing flame	?	?		?	?	?	?	?		?	?
Integration time too small		?	?	?	?				?		?
N2O-acetylene flame	?	?	?	?	?	?	?			?	?
Burner>8 on vertical scale											
No display - HCL on											
Fluctuating display- lamp intensity											
CHEMICAL CONDITIONS											
Sample is viscous										?	
Uptake rate less than 5 mL/min	?					T		T			
Refractory element present											

Table 2. The knowledge matrix in AAdiagnosis.

GP8 **THE PREPARATION OF STANDARD REFERENCE AQUEOUS SOLUTIONS (SRM) FOR HIGHLY HYDROPHOBIC MATERIALS. Barry G.Oliver*, ZENON Environmental Laboratories Inc., 8577 Commerce Court, Burnaby, BC V5A 4N5 and M.Glenys Foster, ZENON Environmental Laboratories Inc., 5555 North Service Road, Burlington, Ontario L7L 5H7**

1.0 Introduction

This study involved the development of standard reference aqueous solutions of highly hydrophobic materials using generator columns. Pioneering work in the area was done at the National Bureau of Standards in Washington by May and several co-workers. As a result of their early work generator columns for several PAHs are available from NBS. The main application of the columns has been to estimate aqueous solubilities and octanol-water partition coefficients of organic chemicals.

The analysis of trace organic in water and effluents is a research area of growing interest. Most analytical techniques are proofed by spiking samples in the laboratory to check recoveries of the various extraction and cleanup steps required to isolate the chemicals of interest from the matrix and from interferences. The weakness of this approach is the lack of knowledge of the stability of the analyte in the sample during the collection, transportation and storage. Generator columns can be used to produce aqueous solutions of hydrophobic organics at known concentrations so that the entire analytical scheme can be tested. These accurate solutions can also be used in interlaboratory studies to test performance of various laboratories.

2.0 Generator Column Preparation

Chromosorb W (60/80 mesh) was used as the column support. The Chomosorb W was first cleaned by placing 2 g of resin in a column and then passing 100 mL of methylene chloride and then 100 mL of hexane through the column at a flow rate of about 10mL/min. The chemical of interest was dissolved in hexane. Two grams of Chromosorb W was then placed in a flask with 100 ml of hexane containing 20 mg of the study compound. The hexane was then removed by rotary evaporation. The support place is thus coated with 1 percent by weight of the study chemical.

The coated Chromosorb W is then packed into a stainless steel column of dimensions, 0.64 cm outside diameter by 25 cm long, using a vibrator to assure tight packing. Both ends were sealed using stainless steel HPLC filter frits and Swagelok fittings. Each column contained about 1 gram of Chromosorb W and 10 mg of the study chemical.

2.1 Column Testing Procedures

Columns were attached to an HPLC pump with a delivery capacity of up to 15 mL/min. The column was suspended in a water both which controlled the temperature to ± 0.1 °C. A variety of flow rates and temperatures were used for column #1 containing hexachlorobenzene (HCB) to study the effect of these variables. Subsequently, an optimum temperature and flow rate were chosen for testing of additional columns. High purity lab water (filtered/carbon absorption/reverse osmosis/ion exchange) was passed through the columns. Volumetric flasks (50 mL or 500 mL) were used to collect the solutions from the column.

2.2 Analytical Procedures

All standards for this study were prepared from high purity crystals obtained from US EPA at Triangle Park, North Carolina. At least 20 mg of crystals were weighed out on a Mettler Model HK60 balance that could be read to ±0.01mg.

Hexachlorobenzene, aldrin and endosulfan the 50 mL aqueous solutions from the columns were then placed in a separatory funnel and extracted with 25 mL hexane. The very low water/solvent ratio assured that greater than 99% of the chemicals were recovered. The hexane layer was dried with anhydrous sodium sulphate and placed in autosampler vials. Four vials from each sample extract were analyzed and the results averaged to obtain each data point. No cleanup or concentration of the extract was performed so no analyte losses would be expected. The analyses were performed using a Hewlett Packard Model 5880A gas chromatograph equipped with an electron capture detector.

3.0 Results

The experimental results from the four study compounds hexachlorobenzene(HCB), aldrin, endosulfan 1 and mirex are compared to literature solubilities in Table 1. In general, agreement between the current generator column produced aqueous solubilities with the available literature solubilities is good.

Table 1. A Comparison of Water Solubilities From This Study to Literature Values* (Concentrations in ug/L).

Chemical	Solubility This Study (20°C)	Literature Solubility	Method	Source
HCB	6.1±0.27	20(?°C)	SF**	Laseter et al(1976)
		6(25°C)	SF**	Metcalf et al(1973)
		47(25°C)	GC***	Miller et al (1984)
		5(25°)	SF**	Yalkowski et al(1979)
Aldrin	23.5±2.8	27(27°C)	SF**	Park and Bruce(1968)
		17(25°C)	SF**	Weil et al(1974)
Endosul. I	470±13	164(?°C)	SF**	Ali(1978)
		150(22°C,pH7.2)	SF**	Phillips(1975)
		260(20°C,pH5.5)	SF**	Phillips(1975)
		530(25°C)	SF**	Weil et al(1974)
		600(?°C)	SF**	MRI(1977)
Mirex	0.048±0.004	1(?°C,0%Salin.)	SF**	Alley(1973)
		0.04(?°C,4%Sal.)	SF**	Alley(1973)
		0.007(?°C)	SF**	Smith et al(1980)

**SF = Shaker Flask Method.

***GC = Generator Column Method.

4.0 Summary and Conclusions

1. Methods for preparing generator columns have been detailed and this technology will be transferred to MOE in a report and through telephone conversations.

2. The aqueous solubilities of HCB, aldrin and endosulfan I have been measured and with the generator columns at 20°C.

3. The effects of flow rate and temperature on these solubility of HCB have been determined.

4. Some preliminary experiments were conducted with mirex and minor difficulties in using the procedure for chemicals with extremely low solubilities were found. These difficulties should be worked out using mirex before moving to the chlorinated dioxin part of the project.

5. Some successful testing was carried out using column with a lower chemical loading 0.05% instead of the usual 1%. This work indicates it may be possible to use much lower amounts of toxic chemicals such as chlorinated dioxins and still produce the desired saturated aqueous solutions.

6. Three generator columns have been delivered to MOE to deliver the following:

Column #1 Hexachlorobenzene(20°C) 6.1 ± 0.27 ug/L
Safe Water Volume = 800 liters

Column #2 Hexachlorobenzene (20°C) 6.1 ± 0.27 ug/L
Aldrin (20°C) 23.5 ± 2.8 ug/L
Safe Water Volume = 200 liters

Column #3 Endosulfan I 470 ± 13 ug/L
Safe Water Volume = 10 liters

GP9

DEVELOPMENT OF AN ENZYME IMMUNOASSAY FOR THE RAPID DETECTION AND QUANTIFICATION OF GLYPHOSATE

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INTRODUCTION

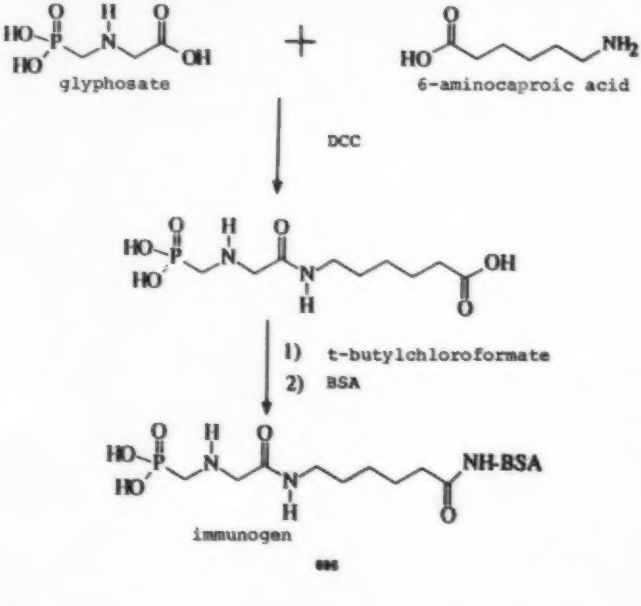
Glyphosate (N-phosphonomethylglycine) is a broad spectrum, non-selective, post-emergence herbicide; it is effective in the control of a wide range of weeds and at the same time is relatively non-toxic to mammals. The LD_{50} based on oral feeding of male rats was reported to be 4320 mg/kg (Watts, 1980). The currently accepted LD_{50} value for mammals is 1568 mg/kg (Miles *et al.*, 1986). Properties which make this compound effective include high water solubility, rapid absorption and translocation by plants, and low degrees of *in vivo* metabolism and degradation. It is a unique compound in that it acts by disruption of phenolic metabolism (Hoagland and Duke, 1981).

Because of the significance of glyphosate, sensitive, accurate and widely applicable analytical methods for glyphosate are essential. Special complexities arise in the quantitation of this compound because it is soluble in water and insoluble in organic solvents. Currently, the detection of glyphosate is most commonly performed by biphasic aqueous-organic extraction followed by cleanup of the supernatant aqueous extract utilizing, first, iron-loaded Chelex 100 resin, and then, AG-1-X8 anion-exchange resin columns. Liquid chromatography coupled to a postcolumn reactor specific for primary amines, or compounds that can be converted to primary amines, is then used for the quantitation of the extract (Cowell *et al.*, 1986). This analytical technique is long , costly, and has a detection limit near 0.05 ppm and recoveries around 80%. The use of an enzyme immunoassay would be of great help in *i*) shortening the time required for the analysis, *ii*) allowing the simultaneous analysis of many samples at the same time, and *iii*) lowering the detection limit. This research project is directed to the development of an enzyme immunoassay against glyphosate using polyclonal antibodies that could possibly, later be replaced by monoclonal antibodies. It is divided into three major stages which include: *i*) the preparation of the immunogen, *ii*) the production and selection of polyclonal antibodies and, *iii*) the preparation of a tracer and the development of a competitive enzyme immunoassay. Currently, part i) and some of part ii) have been achieved.

MATERIALS, METHODS AND RESULTS

1. SYNTHESIS OF THE BOVINE SERUM ALBUMIN-GLYPHOSATE CONJUGATE

As glyphosate is too small a molecule to be immunogenic, the first step in the production of an immunoassay for glyphosate is the synthesis of an immunogen consisting of the hapten, glyphosate, covalently linked to a large carrier molecule such as bovine serum albumin (BSA). The antibodies raised against such an immunogen tend to have highest specificity against that part of the hapten molecule that is furthest removed form the carrier. This consideration caused us to link glyphosate via the carboxylic acid function of the glycine moiety which will allow as much as possible of the phosphonate group to be exposed during antibody production. Molecular modelling calculations that predict the degree of steric hindrance of the hapten and the optimum electronic distributions for antibody formation indicated that the hapten should be attached to BSA via a five to six carbon chain rather than directly.



This was accomplished using 6-aminocaproic acid in the presence of 1,3-dicyclohexylcarbodiimide (DCC) to form an amide. The amide was purified by preparative thin layer chromatography and methanol recrystallization and its identity confirmed by nuclear magnetic resonance and mass spectrometry. The glyphosate-caproic conjugate was attached to BSA by a mixed anhydride method using t-butylchloroformate. The resulting immunogenic conjugate was purified by dialysis against distilled water and subsequent lyophilization.

2. POLYCLONAL ANTIBODY PRODUCTION AND SELECTION

A set of six rabbits was used for the immunization. Blood samples were taken through the ear at DAY 0 in order to obtain pre-immune serum from each of the rabbits. They were then injected with 0.5 mL of a mixture 1:1 of the conjugate in PBS and complete Freund adjuvant (approx. 1 mg/mL). Four (4) injections of 0.5 mL each were made on each animal at the same time, two injections sub-cutaneously and two injections intra-muscularly. On DAY 21, 42, and 63, the rabbits were re-injected with the same amount of conjugate, but this time, mixed 1:1 with incomplete Freund adjuvant. On DAY 73, each rabbit was sampled through the ear and tested for the presence of anti-BSA antibodies using simple immunodiffusion. Since no reaction was observed, the six rabbits were re-injected twice following the same protocol in an attempt to raise the titer. They were then re-tested by immunodiffusion against BSA and also the BSA-glyphosate conjugate. Again, there was no reaction observed between the sera and the BSA alone. However, for two rabbits, precipitation bands were observed between the sera (rabbits number 3 and 6) and the BSA-glyphosate conjugate. These two rabbits were then bled by intra-cardiac puncture. Their sera is now being tested for specificity against glyphosate using a radioimmunoassay (RIA).

The RIA testing of the rabbit sera is as follow. Polyvinyl chloride microtitration plates are coated with 100 µL of a 1,000-fold dilution in PBS (20 mM) of swine anti-rabbit immunoglobulins (Dakopatts, Denmark) and incubated overnight at room temperature (RT). Uncoated plastic is then saturated by adding 100 µL of PBS-BSA (6%) to the wells. After an incubation of 3 h at RT, the plates are washed three times with PBS and 100 µL of serial dilutions, in PBS, of the rabbit antisera are placed in wells. The plates are left at RT for 3 h. They are then washed four times with PBS-Tween 20 (0.05%) (PBST) and filled with 100 µL of ^{14}C radiolabelled glyphosate (approx. 50,000 cpm) in PBST. After 3 h of incubation at RT, the plates are washed six times with PBST and each well is cut and placed in a liquid scintillation vial containing 12 mL of Beckman's Ready Protein^{+} cocktail. Radioactivity present in each well is then estimated using a Packard 1900CA Liquid Scintillation Analyzer. Antibody titer is defined as the reciprocal of the amount of antisera (mL) required to give 50% binding of radioactive glyphosate.

Results were not yet available from the RIA testing when the Proceedings manuscripts were required.

DISCUSSION

The power of immunochemical technology to solve problems in the pesticide field is becoming widely appreciated. Immunoassays are physical assays which offer many advantages, including simplicity, sensitivity and specificity. Immunoassays do not rely on volatility (GC), thermal stability, or the presence of chromophores (UV, fluorescence) or heteroatoms (ECD, NPD) for detection. The development of competitive enzyme immunoassays is one of the most promising approaches to the detection and characterization of both xenobiotics and biological entities. Not only does enzyme immunoassay development allow the lowering of detection limits for environmental pollutants, but it also allows spending less time doing the routine runs and permits its application in less fully equipped laboratories. Since immunoassays usually work well in human body fluids, the technology is applicable to evaluation of worker exposure as well. Thus, immunochemistry is likely to complement existing technologies in providing, at reduced cost, the type of data currently generated in pesticide trace analysis.

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GP10

EXPERT SYSTEM FOR USE IN ENVIRONMENTAL CHEMISTRY. DESIGN AND IMPLEMENTATION OF GC-MSexpert AND AAexpert

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ABSTRACT

Expert systems will play an essential role in the environmental laboratory in the future. In this paper, we describe progress towards the development of two major expert system modules (i) AAexpert, a program that can control an atomic absorption spectrometer and associated solution handling instrumentation, can analyze the quality of the analytical data measured and can provide advice on corrective action to be taken to improve data quality, and (ii) GC-MSexpert, an expert system, which is designed to assist in the interpretation of GC-MS data associated with environmental samples. This system includes structure elucidation, identification of components and GC-MS data processing. Both these programs form part of ACexpert, a rule-based expert system with a graphic user interface written within Microsoft Windows 3.0. ACexpert incorporates several expert systems, including ACselect, AAexpert and GC-MSexpert. This paper describes the design of the prototype for these expert systems and a novel spectral data handling module.

Introduction

Expert system are ideal as tools to help solve complicated practical problems that require considerable prior technical knowledge. Expert systems are able to apply reasoning and problem-solving techniques to solve real-world problems. Applications within analytical chemistry fall into two broad categories: (i) systems that are developed to interpret experimental results, and (ii) systems that provide guidance or advice as to the course of action a analyst should take [1-4]. Specific programs include analysis of IR spectra [5], ^{13}C NMR [6], MS/MS [7], GC/IR/MS [8], methods development in HPLC [9,10] and automated metal analysis [11-14]. The promise in the development of expert systems for use in analytical and environmental chemistry is that the rules and facts in the knowledge base of an expert system can be assessed by experts in both regulatory agencies and industry, and the advice given to a wide body of user can be verified. An advisory role for expert systems appears at present to offer the greatest productivity gains. Typical roles for expert systems involve diagnosing instrument faults, diagnosing problems in instrumental measurements, advising on method development in chromatography, advising on complex data analysis and analyzing databases for hidden trends. These latter examples are of direct interest when environmental monitoring programs require large numbers of measurements to be made at frequent intervals: the quantity of data can overwhelm resources available to the analyst.

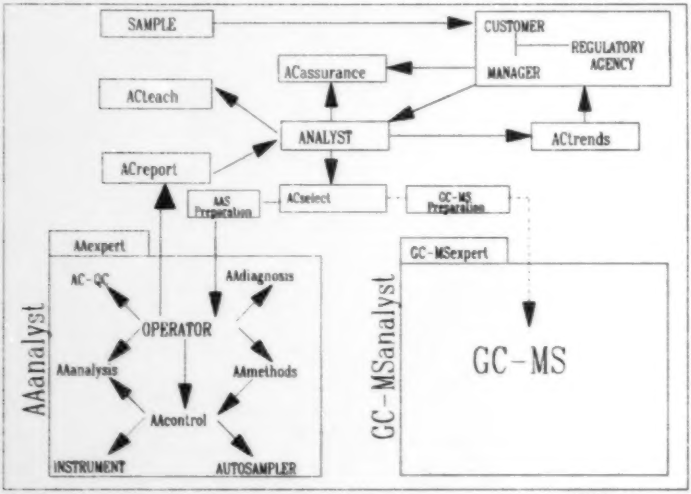
One of the most important aspects of an expert system is the implementation of the user interface. In an advisory role communication between the system and the user must be extremely flexible so that the flow of information is most efficient. We find that the breadth of information needed by the program in order to offer advice when systems are developed for use in the analytical laboratory, requires a very powerful user interface in which the user can monitor and adjust the information currently held by the system in response to the advice offered.

Results and Discussion

ACexpert This system incorporates a number of interrelated modules, of which ACselect can be used to determine the best method to use in the analysis of unknown compounds, and AAexpert and GC-MSexpert are programs that incorporate complete advisory systems. Figure 1 shows the structure of ACexpert.

ACselect ACselect is an expert system that aids in the selection of the optimum analytical technique to be used in the analysis of complex samples. ACselect has been developed by combining the ACexpert user interface with an "analytical techniques knowledge base" through an inference engine provided by the KDS shell. ACselect is subdivided into different sections, for example, AAmethods, which provides detailed information about AAS methods, and GC-MSmethods which provides similar information for analysis by GC-MS techniques. The object of this separation of method selection is that within an analytical laboratory there may be several techniques capable of making the determination. A number of parameters must be considered when the choice is made, amongst these are the required detection limits, freedom from interference due to the supporting matrix, cost per analysis, and regulatory agency requirements.

Selecting a proper analytical method is a more complicated procedure than simply accessing a set of information from the knowledge base. ACselect itself is an expert system, which not only consists of a knowledge base comprising the analytical information, but also a set of rules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GC-MS

Fig. 1. ACexpert

that link these data together. The inference engine matches the users requirements for the sample, such as species, matrix, concentration range etc., with rules in the knowledge base in order to offer advice about the best analytical method. The value of expert system modules like ACselect, is that future regulations concerning environmental protection can be issued as a knowledge base on disk to be used by the managers of analytical laboratories to design monitoring protocols.

AAexpert Trace metal concentration determination using AAS (atomic absorption spectrometry) requires the completion of several tasks, each of which require extensive knowledge and expertise. The demands of regulatory agencies in the area of environmental protection, in particular, are such that precise selection of methods and the implementation of rigorous quality control is essential. Expert systems are ideal under these conditions as the evolutionary changes in methods and regulations can be added to the knowledge base without rewriting the program. Matrix effects, physical interferences, and spectral interferences are among the analyst's expert knowledge that the program must be able to assess as it decides on the advice to offer the user. Although incorporation of an expert system into the analytical laboratory will change how some of these tasks are carried out, the judgement and expertise of an analytical chemist or a skilled technician are still be needed to interpret the information offered by the computer system. The functions of the individual expert systems within AAexpert have been outlined previously [11-14].

EAexpert EAexpert is a complex expert system that controls the results obtained from a series of expert systems that carry out data analysis of data obtained by a number of chromatographic techniques. Figure 2 shows the structure of this expert system. Individual modules carry out data analysis using both spectral libraries and external databases to provide the best suggestion for the identity of the compounds represented by the spectral data. EAmaster then combines the results of each module and determines if a unique compound or class of compound can be identified. In this figure, we show the mix of procedural routines (for example, data conversion from instrumental formats to a common database format and data reduction) and rule-based routines. We briefly describe here the design of the system and features of the GC-MS data analysis module, GC-MSexpert, which is designed to give advice during GC-MS data analysis of measurements made on organic compounds in complicated environmentally-important samples.

Combined gas chromatography-mass spectrometry (GC-MS) is an established technique for the analysis of complex mixtures and because of its sensitivity, wide range of applicability and versatility, the GC-MS technique is widely applied in chemistry, medicine, biochemistry, pharmacology, environmental pollution control, and food science [15]. However, analysis of individual GC-MS data sets generally requires a specialized expertise. In order to deal more efficiently with this problem, GC-MSexpert has been designed as a rule-based expert system with a graphical user interface. There are three stages in our design:

1. Development of GC-MS data processing/data transfer facilities.
2. Implementation of a sophisticated graphical user interface.
3. Design of the knowledge base.

Analysis of GC-MS data can be very complicated and requires extensive knowledge and expertise. Moreover, a GC-MS analysis of samples from environmentally-important sources produces a tremendous amount of data, which requires an effective means of data management and analysis. The prototype described here is designed to resolve these problems. The GC-MSexpert system is designed to assist the analyst deal with the GC-MS analytical problems

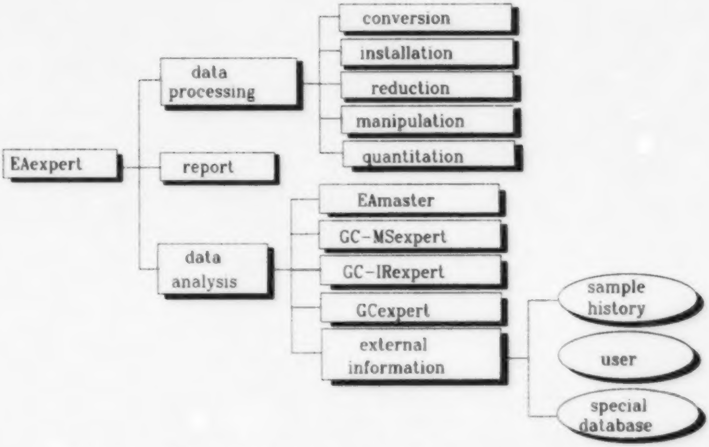

Figure 2. Outline of the EAexpert system

associated with the determination of compounds in the sample of environmental interest, carry out automatic structure elucidation and offer advice on the identification of components in the samples, and finally, provide a sophisticated tool for GC-MS data processing, which includes a spectral data archiving capability for data interchange between laboratories. An overview of the system architecture is shown in Figure 3. The program will act directly to carry out both rule-based and procedurally-based operations on GC traces and associated mass spectral data. The analyst initially can browse through the GC data with the system presenting selected mass spectral data in a graphical window. Baseline subtraction and alignment with data from standards can then be carried out. Band deconvolution, fragment identification and library searches, controlled by the rule-base, are used to identify individual components in the chromatography of the analyte. Usually, if the mass spectrum of a substance of unknown structure has been obtained, the most popular computerized method of determining the structure of the unidentified compound is to search through a library of known spectra for a match between the sample spectrum and that of a compound in the library. When spectral data from the unknown compound are not present in the library, library searching techniques are of limited use. One approach to solve this problem, is to propose a structure that is consistent with the given spectrum. However, it may be possible to propose several structures that are compatible with the spectrum. The proposed structures must be verified by a variety of other methods.

Implementation of the user interface Expert systems generally include a knowledge base, an inference engine and a user interface. The user interface handles all communication between the user and the different modules in the expert system. An appropriate and user-friendly interface is vital for the success of an expert system that is to be used as an advisor. Since the analysis of GC-MS data usually involves complicated data interpretation and significant

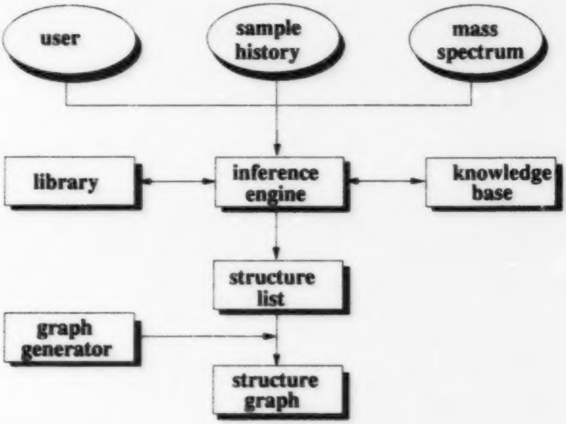

Figure 3. Structure of GC-MSexpert

mathematical processing, the requirements for the user interface include a component to aid in managing the complexity of these tasks. The GC-MSexpert system is implemented within Microsoft Windows™ 3.0, which provides a multitasking, graphical-based windowing environment.

Acknowledgements

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GP11

DESIGN AND IMPLEMENTATION OF ACselect

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ABSTRACT *This paper describes the application of expert system technology to analytical chemistry as part of the development of the ACexpert system. The success or failure of an analysis often critically depends upon the proper selection of a method. ACselect is an expert system that advises the analyst how to solve real-world problems based on sample analysis information. A prototype of ACselect has been developed in our laboratory which encodes the technique for choosing a proper technique for a required analysis. ACselect has been developed by combining the ACexpert user interface with an Instrumental Analysis database through the inference engine provided by the AI shell, KDS. ACselect is a rule-based expert system written within ACexpert system that uses a Windows 3.0™ interface.*

Introduction

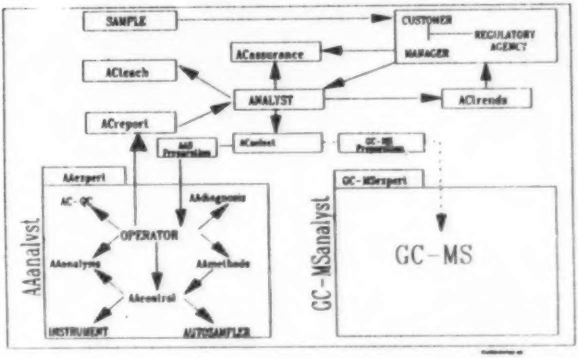
The standard approach to solve an analytical problem is largely heuristic, with past experience and rule of thumb being used. Such rules do not have general applicability and only experience can tell whether or not to apply one in a given situation. Expert system can combine theory with rules to provides the flexibility necessary to cope with complex problems of the real world[1]. These systems will not replace chemists, but rather will assist them in performing their daily work[2].

The development of an expert system must start with some concept of what an "expert" is, how experts perform scientific tasks, and how scientific "expertise" is used by the expert. The unforeseen obstacle in developing expert systems is the difficulty in extracting knowledge from human experts and in representing knowledge in a logical and consistent format. This problem is often referred to as *the knowledge acquisition bottleneck*[15]. The value of our present research is to find a way to extract expertise from human experts and reformat into a rule-based knowledge structure which the computer can use.

Structure of ACexpert

Expert system applications within the field of Analytical Chemistry[3-13] fall into two broad categories: (i) Systems that are developed to interpret experimental results, and (ii) systems that provides guidance as to the course of action the analyst should take.

ACexpert, which is a rule-based expert system with a graphical user interface, has been designed to provide real-time assistance to the analyst in completing a required analysis. ACexpert incorporates several individual expert system modules, including ACselect, AAexpert, and GC-MSexpert (Figure 1). Each of these is capable of acting independently or as a module of the full system.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ACteach
ANALYST
ACtrends
ACreport
AAS Preparation
ACselect
GC-MS Preparation
AAexpert
AC-GC
AAdiagnosis
OPERATOR
AAanalyses
AAmethods
AAcontrol
INSTRUMENT
AUTOSAMPLER
AAanalyst
GC-MSexpert
GC-MSanalyst
GC-MS

Figure 1. The Structure of ACexpert

ACselect

The general stages in an analytical process are: (1) Sampling; (2) Separation and preparation; (3) Selection of an analytical method; (4) Performing the analysis; (5) Quality control/Quality assurance; and (6) Reporting the results. Clearly, this list does not indicate any of the complex interactions that exist between the various steps. Although each of the above steps is almost always involved in an analysis, there is no definitive algorithmic approach that can be applied in every situation.

The expert system shell KDS-3 (KDS Corporation) has been chosen within which our expert system will be developed. As an inductive shell, KDS works in the sequence of facts...rules...knowledge, the "step by step" example-driven programming structure makes KDS an excellent environment for resolving the ambiguity of unclear rationalizations[14].

Selecting a proper analytical technique is more involved than simply accessing a set of information from the database. ACselect itself is defined as an expert system, which not only consists of the knowledge base where all the analytical chemistry information is stored in the form of rules and facts, but also has a built-in inference engine provided by the KDS shell, which matches the requirements of the user through the ACexpert user interface and the proper information selected by the AI shell from the database.

Whenever confronting an analytical problem, an analyst accumulates a set of information before he/she can make any further decisions. This information includes: What is the sample type, such as: inorganic or organic, pure or mixture, elemental or molecular? What is the matrix, or sample media? What is the concentration range? No matter what method is chosen, all these questions must be answered before a correct conclusion can be reached. If F(x,y,z) can be used to represent an analytical case, then we call the unknown factors (x, y, and z) the "Degree of Freedom (DOF)" for this particular analytical problem. Accordingly, ACselect is also broken down into sub-modules, each of which performs a single task, which aims to eliminate one of the DOFs in each analytical problem. A general module holds all these pieces together to form a complete program (Figure 2).

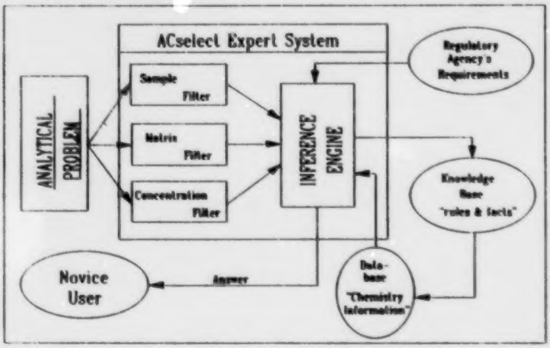
ACselect Expert System
Regulatory Agency's Requirements
Sample Filter
ANALYTICAL PROBLEM
Matrix Filter
INFERENCE ENGINE
Knowledge Base "rules & facts"
Concentration Filter
Novice User
Answer
Data-base "Chemistry Information"

Figure 2. The Structure of ACselect

It is clear that through a series filters, the DOFs become eliminated, and from this point, combined with the requirements of the regulatory agency or the customer, a clear and detailed profile about the sample begins to emerge. This computerized information can then be used by the computer as a direction that the inference engine uses with the rules and facts from the knowledge base to rationalize the generation of the proper method(s) for the novice user.

Discussion

We have completed AAdiagnosis using KDS (see the paper by Lahiri and Stillman) and have developed new techniques with which to code the heuristic knowledge required by ACselect. Although ACselect is mostly still in the design stage, we did try several knowledge modules based on the ideas explained previously. Because the computer program can not "think", the focus really is how intelligent can the program be? ACselect cannot accomplish its task by simply accessing a database. The choice of a technique and subsequently a method is too complicated for that approach. Our study aims at combining rules and database access in one program in order to provide that program the ability to offer expert advise.

Acknowledgement

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GP12

CHARACTERIZATION OF THE EXTENDED CAPABILITIES OF ICP-MS WITH FLOW INJECTION INTO A GASEOUS CARRIER.

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Although one of the features of inductively coupled plasma mass spectrometry (ICP-MS) is its low detection limits for a large number of elements, the quantitative determination of As, Se and Hg at 0.2 µg/L in ground water is a task which is still impossible, on a routine basis. This situation results from several factors. First, all those elements possess a degree of ionization ≤ 50% in the argon plasma (1). Secondly, the plasma produces background peaks directly overlapping three of the six isotopes of Se (at m/z 76, 78 and especially 80), which further hampers its determination since all the remaining isotopes of Se have a relatively low natural abundance. Isobaric interferences from argon-containing polyatomic species may also degrade the detection limit for As if any chlorine-containing compound is part of the matrix since it would lead to the formation of $^{40}Ar^{35}Cl^+$ which directly overlaps the only isotope of As. Finally, Hg possesses six isotopes which all have a natural abundance lower than 30%. The determination of this element is also plagued by a large and persistent memory effect (2) which unduly raises the background unless excessively long wash-out times are used between samples.

In order to enable the simultaneous quantitative determination of these three elements with a determination limit (i.e. 5 to 10 times the detection limit) of 0.2 µg/L, changes in the operating conditions of the instrument are required. Ideally, these changes should result in: 1) an increase in the degree of ionization; 2) a reduction of isobaric interferences from polyatomic species containing Ar; and 3) a reduction in memory effects. Several approaches have been used towards each of these goals but, so far, none has aimed at the three of them simultaneously.

Mixed gas plasmas have been shown to enhance the ionization process (e.g. 3-4). For instance, Lam and Horlick (3) reported that the addition of N^2, air or O^2 to the plasma gas in ICP-MS improved sensitivity at smaller sampling depth, if the nebulizer flow rate and the power were increased. Although in their work and that of others, the other gas was mixed with Ar prior to introduction into the torch, other approaches can also be used. For instance, Murillo and Mermet (4) reported that an addition of H^2 as sheath around the nebulizer gas flow enhanced the ionization process. No matter how the gas is added, the enhancement observed with mixed gas plasmas results from the higher thermal conductivity of molecular gases which provides a more efficient transfer of energy within the plasma (4).

Mixed gas plasmas can also lead to a substantial decrease in isobaric interferences from Ar-containing polyatomic species. For example, Evans and Ebdon (5) as well as Branch et al. (6) reduced drastically the interference from $^{40}Ar^{35}Cl^+$ on $^{75}As^+$ by adding a small amount (30 mL/min) of N^2 to the nebulizer gas flow rate.

Desolvation can be used to further enhance the degree of ionization and reduce interferences from polyatomic species. For instance, Lam and McLaren (7) reported a substantial reduction in $^{40}Ar^{16}O^+$ (which overlaps directly with the major isotope of Fe) by adding N^2 to the plasma gas and desolvating the aerosol prior to its introduction into the plasma. Not only does N^2 scavenge oxygen (6), but the reduced solvent load decreases the amount of energy required for the desolvation process, leaving more energy available for the ionization and/or excitation processes.

As far as memory effect is concerned, the most straightforward way of reducing it is to decrease the amount of sample being introduced into the plasma. Flow injection (FI) is a very convenient and simple way to achieve this (8) since it consists in injecting discrete amounts of sample (for example, 100 µL) in a flow of carrier (typically water). Obviously, aspirating a few microliters of a solution containing Hg cannot lead to as large a memory effect as continuously aspirating the same Hg solution. Furthermore, the carrier which immediately follows each sample plug has a continuous rinsing effect. FI can be used to minimize the memory effect of Hg (2). Moreover, if the distance between the sample injection valve and the nebulizer is kept small, only a limited dispersion of the sample occurs as it moves towards the nebulizer, resulting in little loss of sensitivity (i.e. a factor of 2 at the most, for 100-µL injections (8)) compared to that observed by continuous aspiration. FI also has numerous additional advantages such as: increases sample throughput, drastic reduction of clogging of the interface by deposition of solids on the sampler and skimmer, minimal sample consumption, etc. (8).

In principle, combining the advantages of FI with those of mixed gas plasmas, should fulfil the three requirements. Ideally, desolvation should also be included to truly maximize the benefits from mixed gas plasmas. A straight combination of the equipment required for FI, mixed gas and desolvation can be made, but it results in a somewhat expensive and elaborate set-up including a peristaltic pump, sample injection valve, some tubing and connectors for FI; a gas proportioner (or a sheathing device if the sheathing gas approach is used) for mixing gases and a heating chamber/condenser system for desolvating the aerosol. A much simpler alternative way is to use a gas as the carrier in FI. Besides from being less expensive, this approach has several other potential advantages. In this way, a gas (such as air or N^2) can be introduced directly into the centre of the plasma, which should reduce the amount of Ar sampled from that region and result in a lower background (i.e. reduced interferences due to Ar-containing polyatomic species). Since the gas is used as the carrier, no dispersion of the sample occurs on its way to the nebulizer, so the sensitivity should be at least the same as that with continuous aspiration. Finally, since only discrete aqueous sample plugs reach the plasma, the solvent load in the plasma will be reduced compared to continuously nebulizing aqueous solutions (but not as much as with desolvation).

During this presentation, FI into air as the carrier will be characterized. In particular, the effect of critical parameters such as the nebulizer flow rate, the uptake rate (i.e. the peristaltic pump flow rate) and the size of the sample loop will be considered. Advantages and disadvantages of the system will be assessed. The results will demonstrate that FI into a gaseous carrier not only substantially reduces the solvent load in the plasma, leaving more energy available for ionization of the analytes, but also enhances ionization. The precision (using peak height) is also improved compared to FI in water; and the sampling rate can be even greater than with FI in water.

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GP13

AUTOMATION OF A DUAL OPEN COLUMN CHROMATOGRAPHIC CLEANUP TECHNIQUE FOR SAMPLES CONTAINING CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS

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A technique to automate the cleanup stage of samples analyzed for ultra trace levels (ppq) of chlorinated dibenzp-p-dioxins (PCDDs) and dibenzofurans(PCDFs) has been researched by the Ontario Ministry of the Environment (MOE). The Fluid Management System (FMS - Nortech Controls) replaces a manual two stage open column cleanup technique used in the Dioxin Unit.

The FMS used in the Dioxin Unit at the MOE processes five samples unattended and automatically through a set of two columns. The first contains three treated silica gel packings and the second column contains alumina. Two fractions per sample are collected, the first contains polychlorinated biphenyls (PCBs) while the second fraction contains PCDDs and PCDFs.

This automated system saves the chromatographer a full day in the sample preparation process. When done manually, the dual column cleanup takes two day; one day per column set with a solvent concentration step in-between columns. The FMS will process one sample extract through two columns in one hour. Samples are run in series, so a set of five samples takes five hours. Once all columns are packed and sample extracts and glassware are in place the system is ready to perform the cleanup unattended.

This system has been optimized for dioxin and furan recoveries. These recoveries are equal to or greater than those achieved by manual column chromatography. No carryover has been observed provided column capacity has not been exceeded.

Method

Hand packed silica and alumina columns were placed in the positions shown in Figure 1. The first step in this automated cleanup was to wet the columns with hexane before sample addition. When this task was complete the sample wass taken from a roundbottom flask and placed on the column. After sample addition, clean hexane was pumped from the sovent reservoir into the roundbottom before being eluted through the column. This step rinsed the roundbottom to help maximize surrogate recoveries.

Once all hexane rinses passed through the columns (silica and alumina) the dioxins and furans were present only on the alumina. Any PCB interferences present were removed with the 2% dichloromethane(DCM):hexane (v/v) elution of the alumina column. The PCDDs and PCDFs were then collected by elution with 25%

DCM:hexane (v/v). After collection was complete all of the common lines were flushed with hexane.

All of the steps described were carried out using the FMS which has a microprocessor to control the valve switching as well as the pumping system. Once a progam had been written for each sample the valving control comands were saved and recalled at a later date.

Method development was carried out by spiking clean solvent with a $^{13}C_{12}$-PCDD surogate standard that had a 2,3,7,8 substituted isomer in each of the congener groups from tetra through to octa. The spiked solvent was then run through the columns as described above and the collected fractions were analyzed for recovery of the surrogate standard. Initial analyses were carried out by GC-ECD (Hewlett Packard 5890). Some of the carryover check samples were run by GC-MS (Finn 4500).

Experimental

An optimized mannual method was used as a baseline for setup of the automated method. Recoveries of the PCDDs using the automated method were optimized using the silica columns alone (Table 1) followed by the complete silica/alumina system (Table 2)

Results and Discussion

TABLE 1 Percent Recovery of Spiking Solution on Silica Columns using FMS

Isomer	Volume of Hexane (mL)	
	130	160
$^{13}C_{12}$T4CDD	64	88
$^{13}C_{12}$P5CDD	56	73
$^{13}C_{12}$H6CDD	65	82
$^{13}C_{12}$H7CDD	67	101
$^{13}C_{12}$OCDD	63	75

TABLE 2 Percent Recovery of Spiking Solution on Dual Columns using FMS

Isomer	Volume of 2%DCM:hexane/ 25% DCM:hexane		
	20/50	20/50[1]	20/50[2]
$^{13}C_{12}$T4CDD	87	103	49
$^{13}C_{12}$P5CDD	66	95	56
$^{13}C_{12}$H6CDD	70	107	44
$^{13}C_{12}$H7CDD	102	124	50
$^{13}C_{12}$OCDD	79	103	48

[1] A five minute delay before elution of the alumina column was programed into the method to ensure all of the hexane eluted off the column before addition of the 2%DCM:hexane.

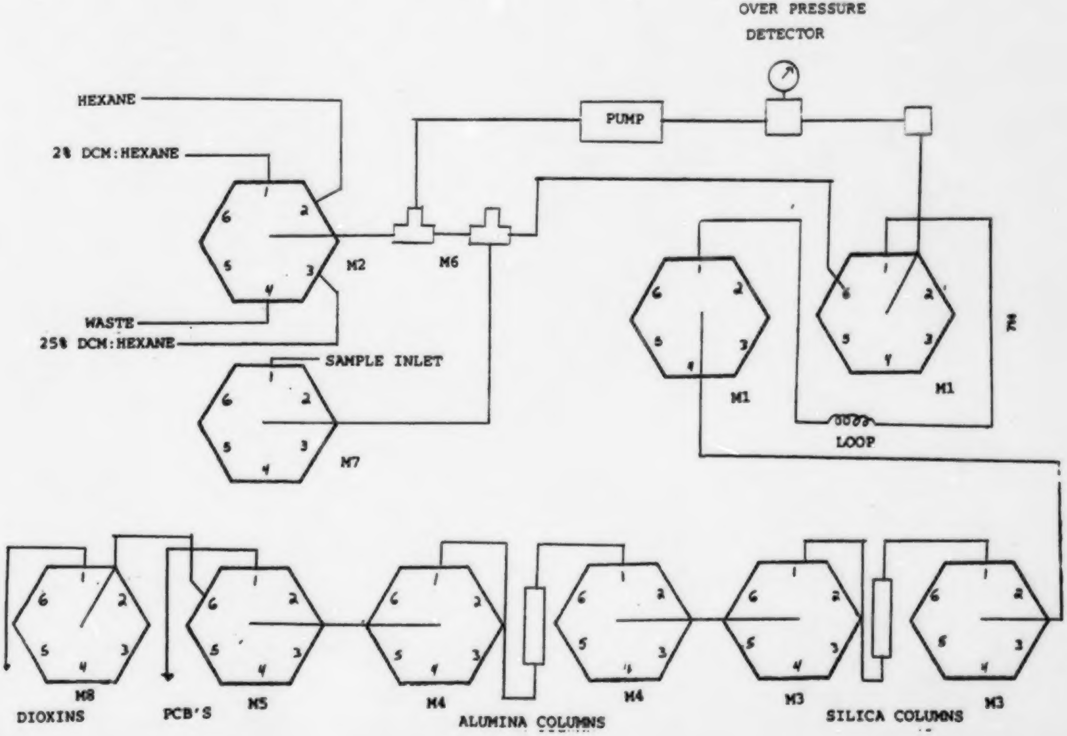
[2] This column set was spiked with a flyash extract as well as the surrogate spike. The levels of dioxins and furans in the flyash were approximately 5 to 50 ng of tetra through octa.

Overall the recoveries are acceptable but should be improved to handle high level samples more efficently. The high levels of dioxins and furans in the sample may have overloaded the columns.

A carryover study was done at the same time. The fraction collected from the column set following the flyash extract contained approximately 0.1 ng of hexa through octa dioxin. This works out to be a 0.2% carryover. If the volume of hexane used to rinse to common lines is increased the carryover may be eliminated.

Fine tuning of the method is still needed. Priliminary results look promising. The advantages to this system are significantly reduced preparation times as well as the reduced human exposure to highly toxic chemicals.

FIGURE 1 AUTOMATED CHROMATOGRAPHIC TECHNIQUE FOR ISOLATION OF CHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS


OVER PRESSURE
DETECTOR
HEXANE
2% DCM:HEXANE
PUMP
M2
M6
WASTE
25% DCM:HEXANE
SAMPLE INLET
M7
M1
M1
LOOP
M2
M8
DIOXINS
PCB'S
M5
M4
ALUMINA COLUMNS
M4
M3
SILICA COLUMNS
M3
1
2
3
4
5
6

GP14

AN AUTOMATED HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC CLEANUP PROCEDURE FOR THE DETERMINATION OF CHLORINATED DIBENZO-P-DIOXINS AND CHLORINATED DIBENZOFURANS

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Introduction

The need for detection of ultra-trace levels of chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) has become a priority in environmental labs because of the possible human health concerns of the 2,3,7,8-chlorine substituted dioxin and furan congeners. CDDs and CDFs occur as byproducts in the manufacturing and combustion of various chlorinated compounds such as chlorinated phenols (eg. pentachlorophenol, which was used on a large scale in fungicides and wood preservatives), phenoxy herbicides, chlorinated diphenyl ethers, and polychlorinated biphenyls(1). The introduction of these pollutants into our waterways from industrial sources is evident when analyzing various biota samples.

CDDs and CDFs bioaccumulate readily in animal fat tissue because of their lipophilic nature and stable physical properties(2). Other chlorinated organic compounds are present in many samples at concentrations several orders of magnitude higher than those for CDDs and CDFs. To obtain acceptable detection levels, this particular analysis requires very sensitive and specific analytical techniques. After extraction of the analytes from the matrix, the bulk of the interferences are removed with an initial cleanup of the sample extract. An important class of interferences are chlorinated diphenyl ethers(CDPEs)(3)(4). These compounds fragment under electron ionization conditions in the mass spectrometer ion source to form ions isobaric with CDF molecular ions, producing false positive results. Low-resolution, high-resolution, or tandem mass spectrometers (LRMS, HRMS, MS-MS) cannot distinguish the CDFs from the CDPEs. Therefore the CDPEs must be removed prior to the GC/MS analysis. The Ontario Ministry of Environment (MOE) has developed a sample preparation procedure incorporating an automated dual column HPLC cleanup step to address this specific interference and this development allows the sample to be analyzed by LRMS techniques.

Experimental Section

Sample Preparation

Twenty grams of ground and homogenized fish tissue was weighed into an Erlenmeyer flask. Each sample was spiked in the flask with a surrogate standard solution containing five 2,3,7,8 substituted $^{13}C_{12}$-labelled dioxin isomers, one from each congener group. The sample was then digested overnight (approximately 16 hours) in concentrated hydrochloric acid. The acid digested tissue was extracted with hexane and the extract was passed through a cylindrical funnel packed with anhydrous sodium sulphate and sulphuric acid impregnated silicic acid. The extract was concentrated and quantitatively transferred to a 100 uL conical vial and taken to dryness. The sample was then reconstituted in 150 uL of hexane and was ready for injection onto the HPLC system.

Instrumentation

The automated HPLC cleanup procedure involves the use of a column-switching step whereby the CDD and CDF fraction is trace-enriched from a neutral alumina HPLC column onto another HPLC column packed with a carbon-silica mixture. The CDDs and CDFs are retained on the carbon-silica column while interferences such as polychlorinated biphenyls, polychlorinated diphenyl ethers, and some polychlorinated napthalenes are not retained. The CDDs and CDFs are recovered from the carbon-silica column by backflushing the column with toluene. The automated HPLC system consists of the following components, all of which are computer-controlled:

-Automated sample processor and injector
- Gilson model 232-401
-HPLC pumps (3) - Gilson model 302 piston pumps
- only 2 are used for forward elution
- solvent used is hexane and dichloromethane
-Programmable HPLC pump
- Gilson Model 305
- solvent used is toluene
-Ultraviolet Detector
- Gilson Model 116 - programmable
- Fraction collector
- Gilson Model 202
-Dynamic Mixer - Gilson Model 811B
-Manometric module - Gilson model 802C
-6-port switching valves (2)
-HPLC columns (2) - Normal Phase Alumina, (0.46 cm ID x 25.0cm from Phenomenex, Torrance, CA, USA), Spherisorb with 5 micron particles

- Empty Waters guard column (0.46 cm x 3.0 cm) packed in-house with a mixture of 5%(w/w) Amoco PX-21 carbon/silicic 70-230 mesh)

After HPLC cleanup, the samples were concentrated and quantitatively transferred to 100uL conical vials. The samples were then ready to be analyzed by the following gas chromatography/mass spectrometry techniques.

Gas Chromatography Low Resolution Mass Spectrometry (GC/MS)

Fifteen fish samples were analyzed using a Finnigan 4500 GC/MS. Samples were introduced onto a 30m DB-5 fused silica capillary column(0.25mm I.D. with 0.25µm film thickness) via an on column injector at ambient temperature. The GC conditions were as described previously(5). The GC effluent was directly interfaced to the mass spectrometer. The instrument was tuned using perfluorotributylamine(PFTBA).

CDD's and CDF's were detected using selected ion monitoring (SIM) techniques. The ions monitored for the native CDDs/CDFs correspond to the three most abundant molecular ions. Only two ions are monitored for the $^{13}C_{12}$-labelled surrogate standards. Two ions are also monitored with each congener group for the CDPEs.

Gas Chromatography Tandem Mass Spectrometry (GC/MS/MS)

Twenty five fish samples were analyzed using a Finnigan TSQ70 GC/MS/MS. The samples were injected on a 60m DB-5 column (0.25mm I.D. with 0.25 µm film thickness), through a splitless injector, at 300°C. The GC was programmed as follows: hold initial column temperature at 120°C for 1 minute, ramped at 7.5°C/min. to 250°C, then ramped to 300°C at 2.5°C/min., and hold for 10 minutes. The carrier gas was helium, at a column head pressure of approximately 22 PSI. As previously described(6), the instrument was tuned using CDDs.

The interferences which affect LRMS sensitivity and selectivity are those compounds which are co-extracted with CDDs and CDFs and are not removed in the cleanup steps. MS/MS can be used to distinguish CDDs and CDFs from chemical interferences by selected reaction monitoring (SRM) techniques. MS/MS detection consists of the mass selection of a parent ion in the first mass analyzer, fragmentation of this ion by collision induced dissociation(CID) and final detection of the daughter ion in the second mass analyzer. Interferences such as CDPEs can not be distinguished from CDFs by MS/MS or any other type of mass spectrometry because under EI conditions they fragment to form ions isobaric with CDF molecular ions in the ion source.

Results and Discussion

The automated HPLC dual column cleanup method developed at MOE was found to be very effective in removing interferences such as PCBs and CDPEs. The recoveries of the internal standards were found to be acceptable and consistent, with a 62% average recovery. The extract was clean enough to allow the analysis to be carried out by LRMS techniques. The detection limits achieved by the Finnigan 4500(LRMS) were typically 4 to 5 PPT. Although these were good detection limits, a detection limit of 4 PPT is required to obtain "Toxic equivalent" detection limits below the levels required for a warning to be issued in the MOE/MNR "Guide to Eating Ontario Sports Fish". The sensitivity of MS/MS techniques was preferred because the detection limits achieved by LRMS were too close to the guideline. The detection limits obtained by MS/MS analysis were typically less than 3 PPT.

Further development will test the applicability of this cleanup procedure to other environmental matrices where CDPEs and other organic interferences are problems. Future work will also include the determination of the active lifetime of a carbon column and optimize the column for maximize lifetime.

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OP15

A STUDY OF CHEMICAL INTERFERENCES IN THE ANALYSIS OF N-NITROSODIMETHYLAMINE IN ENVIRONMENTAL SAMPLES.

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N-nitrosodimethylamine (NDMA) is also known as dimethylnitrosamine (DMNA) and N-methyl-N-nitrosomethanamine. NDMA can be present as a trace contaminant in industrial processes and in products manufactured using dimethylamine. It may also be found in various foods such as cured or smoked meats, beverages such as beer and in tobacco smoke condensates. In addition, NDMA has been found in some ion exchange resins. NDMA has been found to be carcinogenic in the mouse, rat, hamster, guinea-pig, rabbit and rainbow trout and is a suspected human carcinogen. Because of the suspected toxicity and carcinogenicity of NDMA, the interim drinking water guideline has been set by the Ontario Ministry of the Environment (MOE) at 9 ppt.

NDMA can be analyzed by a number of methods including gas chromatography (GC) followed by thermal energy analysis (TEA), low resolution mass spectrometry (LRMS) or high resolution mass spectrometry (HRMS).

The sensitivity of the instrumentation is sufficient to meet the drinking water guideline. However, the degree of selectivity required of the detection system may be predicated by the degree of sample cleanup utilized.

The sample preparation protocol developed at MOE was designed to be simple. Since NDMA is a neutral compound, the sample cleanup, after extraction from the matrix, is a partitioning scheme that removes the basic and acidic components from the extract. A summary of the protocol is outlined below:

d_6-NDMA is added to the sample as the internal standard. Filtration is used to remove any particulates that may be present. After the pH is adjusted to 12 to keep the acidic components in the aqueous phase, the basic solution is serially extracted with dichloromethane. The dichloromethane extract is washed with a sulphuric acid solution to remove basic components from the organic phase. The washed extract is filtered through granular anhydrous sodium sulphate to remove water and is then concentrated by rotary evaporator and a nitrogen evaporating unit.

The sample extract contains the remaining neutral organics and no further cleanup is done to separate neutrals from neutrals.

The sample extracts were analyzed by GC/LRMS and GC/HRMS.

The mass spectrum of NDMA consists of 2 major ions, the molecular ion at m/z 74 and an intense fragment ion at m/z 42. Selected ion monitoring (SIM) analysis of NDMA by GC/LRMS was limited to a quantitation ion at m/z 74 and a single qualifying ion at m/z 42. The acceptable ratio of m/z 42:74 was set at +/- 20% of the ratio obtained from a calibration standard run on the same instrument.

The mass resolution requirements for HRMS were determined as follows:

The exact masses for NDMA and a common ester fragment are m/z 74.0480 ($C_2H_6N_2O$) and m/z 74.0368 ($C_3H_6O_2$), respectively. The mass resolution required to differentiate these masses is 6,607 [74/(74.0480-74.0368)]. Operation of a high resolution mass spectrometer at 7,000 resolving power (RP) allows NDMA to be differentiated from chemical interferences such as $C_3H_6O_2$.

On a single quadrupole mass spectrometer, which is restricted to low resolution mass spectrometry (LRMS), ions having the empirical formulae $C_2H_6N_2O$ and $C_3H_6O_2$ are indistinguishable from each other because they both have m/z = 74. Therefore qualifying ion(s) must be used and the ratio of the qualifying ion to the quantitation ion must be within acceptable limits.

On a high resolution mass spectrometer, single ion monitoring of the accurate mass m/z 74.0480 provides sufficient selectivity to distinguish NDMA from chemical interferences.

Instrumental conditions were as follows:

	GC/LRMS	**GC/HRMS**
GC	HP5890	Varian 6000
MS	VG Trio-2 or HP 5970 MSD	VG ZAB-2F
Column	DB-1701 (30 m)	DB-1701 (30 m)
Electron energy	70 eV	70 eV
Ions monitored	m/z 42, 74 (NDMA) m/z 46, 80 (d_6-NDMA)	m/z 74.0480 (NDMA) m/z 80.0857 (d_6-NDMA) m/z 68.9952 (PFTBA)(lockmass)

Analyses of drinking water samples were undertaken. A comparison of analyses of drinking water extracts is shown in the following table:

LRMS vs HRMS Data (ug/L)

Sample	**LRMS-A**	**LRMS-M**	**HRMS**
1.	0.025	0.016	0.019
2.	0.023	0.015	0.012
3.	0.017	0.011	0.011
4.	—	0.011	0.013
5.	—	0.034	0.019

A = automatic areas
M = manual areas

These data demonstrate that:

(1) automatic areas are dependent on the peak/baseline detection parameters chosen and the peak widths of overlapping interferences; peak areas may have to be determined manually (compare samples 1-3).

(2) neutral chemical interferences in drinking water samples co-elute with NDMA.

(3) confirmation by HRMS may be required.

Further studies included other matrices as shown in the following table:

LRMS vs HRMS Data (ug/L)

Sample	**LRMS**	**HRMS**
1. Spiked HPLC-grade water	0.49*	0.42
2. STP influent	0.43	0.40
3. STP influent	0.11*	0.02
4. STP influent	0.20*	0.24
5. Groundwater	ND	0.09
6. Groundwater	1600*	170
7. Industrial effluent	0.37*	0.26

* interference (incorrect ratio of m/z 42:74)
ND = not detected (no peak)

These data demonstrate that:

(1) neutral chemical interferences in other matrices co-elute with NMDA.

(2) confirmation or analysis by HRMS may be required.

Full scan GC/LRMS of a groundwater (sample 6) was undertaken to identify some of the neutral chemical interferences.

Chlorobenzene, ethylbenzene and xylenes were found to be present. Chlorobenzene and ethylbenzene co-elute with NDMA and d_6-NDMA. The xylenes elute after NDMA but can co-elute if present in sufficient concentrations.

These compounds have minor ions at m/z 74 and will interfere with the m/z 74 of NDMA. The mass resolution required to differentiate them from NDMA is 2,285. Operation of the HRMS at 7,000 RP is sufficient for this differentiation.

With the present level of sample cleanup, the ratio of m/z 42:74 that is used as a criterion for positive identification of NDMA by LRMS is of limited utility because it is frequently outside of the +/- 20% window even in relatively clean samples such as drinking water or laboratory procedure blanks. In some cases, this is due to interferences at m/z 42. However, interferences can also be detected at m/z 74 or m/z 80. In these cases, the quantitation will be adversely affected. For LRMS to be a viable technique, a more rigorous sample cleanup (separation of neutrals from neutrals) and possibly better chromatography are necessary.

Single ion monitoring by LRMS does not afford sufficient selectivity for a positive identification of NDMA. Therefore, a protocol that utilizes a minimum number of sample preparation steps requires confirmation, or analysis by HRMS for positive identification and accurate quantitation.

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A Turn-Key FTIR System for the Analysis of Gas Phase Polychlorinated Biphenyls

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Abstract

A turn-key gas phase polychlorinated biphenyl analysis system has been developed using Fourier transform infrared spectrometry, artificial intelligence assisted library searching and an automated infrared interpreter. Vapor phase infrared spectra of 37 PCB isomers have been measured and used to define the interpretation rules. The library search algorithm and the infrared interpreter take advantage of the portability, computing power and mass data storage capability of PC/DOS systems and is demonstrated to be a cost effective tool to ensure consistent data interpretation. This turn-key system allows for rapid identification of complex PCB mixtures with elucidation of contributing PCB congeners.

Introduction

An automated infrared interpreter (PAIRS $^{+}$) was developed on an IBM personal computer (PC) running under the Microsoft disk operating system (DOS). Details of this program and its application for the analysis of oils and greases is given elsewhere (1). Briefly stated, PAIRS $^{+}$ combines both artificial intelligence and library search capabilities to interpret the infrared spectra measured with a wide variety of spectrophtometers. The library search subprogram uses five main algorithms: absolute difference (AB); square of absolute difference (SQ); absolute difference of first derivative (AD); square of difference of first derivative (SD) and time domain cross correlation (FT). A sixth additional algorithm, the combined algorithm (CO) was developed combining the library search results from the first five algorithms resulting in a higher confidence level for the reported data.

An artificial intelligence approach to gas phase PCB analysis in PAIRS[*] has been devised which can identify different types of chlorinated benzene rings based on the position, intensity and full width at half maximum (FWHM) of the infrared bands in the spectrum. These information have been obtained from the spectra of 37 PCB isomers that we have measured. With the combination of a suitable GC column, appropriate GC experimental conditions and this program it may be possible to identify all 209 PCB isomers which may be present in the sample.

Experimental

Solutions of 37 individual PCB isomers (Ultra Scientific, Wellington, CIL) were prepared in iso-octane with an initial concentration of between 100-150 ppm. Table 1 gives the list of these PCB isomers. Solutions were further concentrated if the S/N ratio of the infrared spectrum was less than 5. A Nicolet 5SX (Madison, WI) FT-IR spectrometer equipped with an air cooled nichrome wire source and a medium range cryogenic HgCdTe detector (cut-off frequency at about 600 cm^{-1}) was used to measure the GC/FT-IR spectra. The gas chromatograph used was a Hewlett-Packard 5890 (Palo Alto, CA) equipped with an on column injector, a wide bore column (cross-linked methyl Silicon Gum, 25 m x 0.32 mm i.d. x 1.0 micrometer film thickness) and a flame ionization detector. The starting temperature on GC for di-, tri-, and tetra- isomers was set at 200 °C and for penta- and hexa- isomers it was set at 210 °C. An initial hold time of 0.5 minute on GC was used and temperature was ramped at a rate of 3 °C/min to 270 °C. The injector temperature was set at 250 °C. The dimensions of the light pipe used were 12 cm x

0.1 cm and was operated at 270 °C throughout the experiment. Interferograms were collected at a sampling rate of 50 kHz, obtaining infrared spectra with 8 cm^{-1} resolution. The Gram-Schmidt orthogonalization algorithm (2) was used to reconstruct gas chromatograph from the interferograms and the infrared spectra.

Results and Discussion

The structure of each polychlorinated biphenyl consist of two benzene rings in which one to ten hydrogen atoms can be substituted by chlorine atoms. Substitution of these chlorines will give rise to eighteen (including a benzene group for PCBs with one unsubstituted ring) different types of chlorinated benzene rings. For example when one chlorine atom is present in the structure of the PCB, three different isomers i.e., 2-mono, 3-mono, and 4-mono biphenyls are possible. When two chlorines are present, 6 different isomers i.e., 2,3-di, 2,4-di, 2,5-di, 2,6-di, 3,4-di and 3,5-di are possible etc. These eighteen types of substitutions give rise to different infrared bands in the spectral region 600 to 2100 cm^{-1}. Figure 1 illustrates the spectra for three of the 37 isomers. Using the 37 spectra, the characteristic infrared bands for each type were identified. The eighteen types of substitution and the characteristic infrared bands are given in Table 2. For each infrared band the averaged normalized intensity and the averaged estimated FWHM are given in the parenthesis. Each PCB isomer is a binary combination of any of these eighteen groups. For some groups the characteristic bands overlap, but at least one band for each group can be identified which is unique to that group.

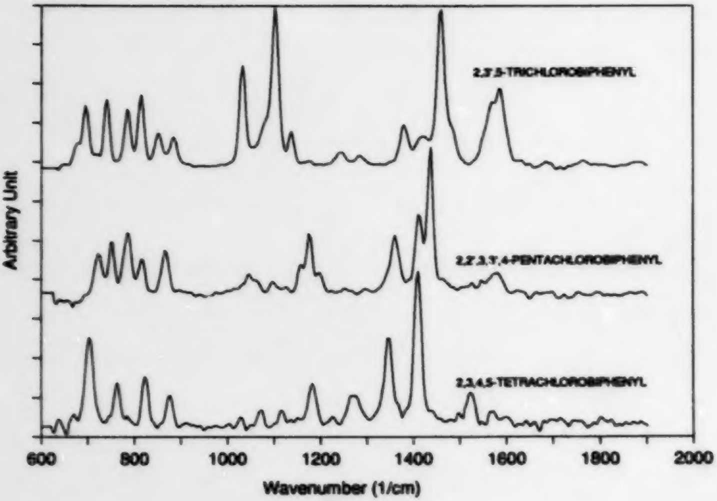

Fig. 1. Infrared gas phase spectrum of three PCB isomers.

Using the information given in Table 2, a program was written to interpret the data and identify the PCBs. This program requires three sets of information: 1) the spectral region of the bands pertinent to each group of PCB isomers where the algorithm will allow for the variations due to the types and the interaction between the two benzene rings, 2) a normalized intensity range from 1 to 10 where the bands will be considered as "weak" for the intensities in the range 1-2, "medium" between 3-6 and "strong" for the intensities between 7-10 and 3) an allowable range for the variation in the full width at half maximum (FWHM) of the bands which will classify the bands as "sharp" for FWHM < 15 cm^{-1}, "medium" for FWHM of 15-30 cm^{-1} and "wide" for FWHM > 30 cm^{-1}. These information have been obtained from the analysis of the 37 vapor phase spectra of PCBs (see Table 2) and can be modified and/or changed in the program as required.

Conclusion

Gas phase infrared spectra of 37 PCB isomers have been measured and analyzed. The information obtained from these spectra are used in the elucidation of PCBs. Since these 37 isomers represent all the possible eighteen different types of substituted benzene rings in the polychlorinated biphenyl structure, it may be used to identify all 209 possible PCB isomers. This technique offers the possibility of direct environmental analysis by remote sensing and the potential for simplified analytical methodology through elimination of clean-up steps.

References

1. M.J. Yang and P.W. Yang, Appl. Spectrosc., in press (1991).
2. L.V. Azarraga and D.A. Hanna, GIFTS, Athens GC/FT-IR Software User's Guide, US EPA/ERL, Athens, GA, 1979.

Table 1- List of PCB isomers measured

Dichlorobiphenyls

1) 2,2'
2) 2,4'

Trichlorobiphenyls

3) 2,2',5
4) 2,3,4
5) 2',3,4
6) 2,3',5
7) 2,4,4'
8) 2,4,5
9) 2,4',5

Tetrachlorobiphenyls

10) 2,2',3,4'
11) 2,2',4,4'
12) 2,2',3,5
13) 2,2',3,5'
14) 2,2',4,6
15) 2,2',5,5'
16) 2,2',5,6'
17) 2,3,3',4
18) 2,3,4,4'
19) 2,3',4,4'
20) 2,3,4,5
21) 2',3,4,5
22) 2,3',4',5
23) 2,3',5,5'
24) 2,4,4',6
25) 2,3,5,6
26) 3,3',4,4'

Pentachlorobiphenyls

27) 2,2',3,3',4
28) 2,2'3,4,4'
29) 2,2',3',4,5
30) 2,2',3,4,5'
31) 2,2',4,5,6
32) 2,3,4,5,6
33) 2,3,4,4',5
34) 2'3,4,4',5

Hexachlorobiphenyls

35) 2,2',3,3',4,4'
36) 2,2',3,3',4,5
37) 2,2',3,3',5,6

Table 2- Characteristic infrared bands for different types of substituted benzene rings.

Type of Substitution	Characteristic ir band(s)
2	751(8[a],17[b]), 1038(4,18)
3	740(5,15), 783(4,19)
4	823(5,22), 1012(3,16), 1094(8,19)
2,3	726(5.20), 1409(7,21)
2,4	821(6,18), 869(2,20), 1103(6,18)
2,5	815(6,18), 1097(8,24), 1376(3,20)
2,6	783(9,27)
3,4	1035(6,22), 1134(6,24)
3,5	806(7,23), 1099(6,15), 1562(10,11)
2,3,4	784(5, 21), 817(4,19), 1174(4,21), 1358(4, 23)
2,3,5	1034(8,23), 1095(9,30)
2,4,5	886(4,20), 1045(4,28), 1091(4,23), 1139(4,23)
2,4,6	838(8,18), 1543(6,23), 1577(7,26)
3,4,5	810(5,19), 876(2,19)
2,3,4,5	1179(4,23), 1342(6,23)
2,3,5,6	1062(8,21), 1388(10,31)
2,3,4,5,6	1323(7,27), 1377(6,19)
Benzene ring	699(7,22)

[a] Intensity on the scale of 1 to 10, 1 being weakest and 10 being the strongest peak.

[b] Full Width at Half Maximum (FWHM).

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